STUDIES ON NATURAL ION EXCHANGERS WITH SPECIAL REFERENCE TO SOIL POLLUTION

SUMMARY

THESIS SUBMITTED FOR THE DEGREE OF

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BY

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S U M M A R Y

SUMMARY

Ion exchange is a standard analytical tool and is widely used in separation science. In laboratories ion exchangers are being used as an important tool to solve new problems, such as rapid and accurate determination of the constituents of a sample, contaminants of alloys, biological substances etc. Ion exchange has also been established as a powerful technique in the field of soil analysis thus proving its worth in soil pollution control.

Soil provides us a place to live and is a reservoir of minerals but with accelerating growth of the world's population and rapid urbanisation tremendous pressure has been created on it. Dumping of industrial wastes containing poisonous chemicals and spraying of pesticides aiding agricultural production and health protection leads to large scale soil pollution. When the soil comes in contact with these chemicals its physico-chemical and biotic properties are affected leading to its degradation and pollution.

The work embodied in this thesis comprises of five chapters. Chapter I is general introduction covering the background of the work presented in this thesis.

Ion exchange is a wide spread phenomenon and ion exchange processes are useful in separation, removal and recovery of various kinds of species. Looking towards the growing interest in the chemistry of the ion exchange process emphasis has been given to the adsorption studies on an ion exchanger and its thermodynamics. To understand the nature of adsorption, in the most convenient way adsorption isotherms are plotted.

The second chapter deals with the equilibrium studies for the sorption of cobalt(II) on two types of soils, performed at 30°C and 50°C by batch technique. The sorption data are analyzed in terms of sorption isotherms, the Langmuir equation and the distribution coefficient Kd. Various thermodynamic parameters, such as thermodynamic equilibrium constant (K_o), standard free energy ($\Delta G°$) changes, standard enthalpy ($\Delta H°$) changes and standard entropy ($\Delta S°$) changes are evaluated. The adsorption data are in close agreement with the Langmuir equation at both temperatures. Sorption of cobalt(II) is higher in Bhopal soil than in Tehri soil and adsorption is lower at higher temperature in both soils.

The third chapter deals with the adsorption studies of pesticide, endosulphan on uncontaminated sandy loam (Mukteshwar) and silt clay loam (Bhopal) soils in acetone-water and methanol-water mixtures, at different volume fractions of cosolvents, performed by batch technique. Higher adsorption of endosulphan was observed on sandy loam (Mukteshwar) soil than silt clay loam (Bhopal) soil and was anticipated with Freundlich constant K values and partition coefficient K_D values. The K and K_D values also confirm that adsorption of endosulphan was higher in acetone-water mixtures than methanol-water mixtures and adsorption decreases with increase in volume fraction of cosolvents (acetone, methanol). The data obtained were used to evaluate the cosolvent theory for describing adsorption of endosulphan in acetone water and methanol-water mixtures. The aqueous phase partition coefficient K_{DW} (mol/g) normalised on fraction of organic carbon of respective soils (f_{oc}), for endosulphan was evaluated by extrapolating $f_s = 0$.

The fourth chapter deals with the effects of exchangeable ions, H^+ and Na^+, organic matter, non-ionic and anionic surfactants and temperature on the adsorption of endosulphan on two different soils. Adsorption studies were performed by batch technique

and adsorption isotherms were in close agreement with the Freundlich equation. The amount of endosulphan adsorbed in all cases was higher in sandy loam (Mukteshwar) soil than in silt clay loam (Bhopal) soil. The adsorption on both the soils followed the order - Hydrogen saturated soil > Sodium saturated soil > Natural soil at 10°C > Natural soil at 20°C > Soil with 0.1% non-ionic surfactant > soil from which organic matter was removed > Soil with 0.1% anionic surfactant > Natural soil at 40°C and was in accordance with Freundlich constant K values and distribution coefficient Kd values. The adsorptive capacity of endosulphan for organic matter and clay content for both soils (natural form) was also evaluated by calculating K_{om} and K_c values. Various thermodynamic parameters such as the thermodynamic equilibrium constant (K_o), standard free energy ($\Delta G°$) changes, standard enthalpy ($\Delta H°$) changes and standard entropy ($\Delta S°$) changes were calculated in order to predict the nature of isotherms.

The fifth chapter deals with the movement of selected pesticides in different soils and their different forms. Movement of pesticides has been estimated by using thin layer chromatcgraphic technique

and has been expressed in terms of R_f values. The R_f values for different pesticides keeping the same solvent system on the different soils follow the order - Mukteshwar < Doiwala < Tehri < Aligarh < Jhansi < Pilibhit. The difference in the movement of pesticides is because of the nature and properties of the pesticides and on certain soil properties such as organic matter content, clay content, texture and structure of the soil, porosity, pH and cation exchange capacity of the soil.

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D E D I C A T E D

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CERTIFICATE

This is to certify that the work embodied in this thesis entitled **"Studies on Natural Ion Exchangers with special reference to Soil Pollution"**, is original work carried out by **Mr. S.M. Umar Iraqi** under my supervision and is suitable for submission for the award of Ph.D. degree in Chemistry of this University.

J P Rawat

(Prof. J.P. Rawat)

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CHAPTER I

INTRODUCTION

Ion exchange is one of the most versatile techniques of separation science. It is at present a standard analytical tool and is widely used in inorganic, organic and biochemical separations. In laboratories ion exchangers are being used as an important tool to solve new problems. Rapid and accurate determination of the constituents of a sample or contaminants of alloys, biological substances and fission products of radioactive elements has become possible by the use of ion exchangers. The use of ion exchangers on large scale may provide mankind with pure water and may be useful for the concentration and extraction of important metals and raw materials which are becoming more and more difficult to produce. Ion exchange has also been established as one of the most powerful techniques in the field of soil analysis thus proving its worth in soil pollution control.

Ion exchange was first reported by the name of base exchange nearly 150 years ago when an English land owner H.S. Thompson became interested in studying the loss of ammonia from manure heaps. He engaged a York Scientist named Spence to investigate this loss. Spence discovered this loss as an exchange

process between calcium (from soil) and ammonia (from manure).

$$Ca\ (soil) + (NH_4)_2SO_4 \rightleftharpoons NH_4\ (soil) + CaSO_4 \quad ..(1)$$

Spence reported his discoveries to the Royal Agricultural Society [1]. These were further confirmed by another agricultural chemist G.T. Way [2] who described this exchange by the name of base exchange. This phenomenon could not be elaborated further as much was not known about the ionic nature of solutions and the crystal structure and composition of the clay minerals present in the soil. Many hypotheses were given to explain this exchange in soils [3] but ultimately it was traced mainly due to the presence of aluminosilicates [4]. The two principal causes responsible for ion exchange property of soils are organic matter and clay minerals [5,6]. The soils rich in organic matter contain humins and humic acid which on decomposition produce a wide variety of organic species, possessing - OH or -COOH groups. These groups are responsible for the ion exchange property in such soils. The soils which do not contain much organic matter also possess a considerable ion exchange property due to

the presence of crystallographic surfaces (clay minerals) with exchangeable sites.

Ion Exchange in soils is a reversible process. Of the two phenomena, cation and anion exchange, the first is generally considered to be more important since the anion and molecular retention capacity of most agricultural soils is much smaller than the cation retention capacity. This property of cation exchange is one of the major distinguishing features between soils and other plant rooting media. Because cations are positively charged, they are attracted to surfaces that are negatively charged. In the organic fraction these arise from the dissociation of H^+ from certain functional groups particularly from carboxylic (-COOH) and phenolic ($-C_6H_4OH$) groups.

$$-COOH \rightleftharpoons COO^- + H^+ \qquad .....(2)$$

$$-C_6H_4OH \rightleftharpoons -C_6H_4O^- + H^+ \qquad .....(3)$$

The carboxylic and the phenolic groups dissociate leaving a negative charge at the site of the functional groups (equations 2 and 3). It is estimated that 85 to 90% of the negative charge of

humus is due to these two functional groups. Two other groups enol (-COH = CH) and imide (=NH) also contribute to the negative charge of the organic matter. Negative charges in the clay fraction generally arise from two sources. The first is isomorphous substitution in layer silicate minerals and the second is caused by the deprotonation of both (i) hydroxyl groups (-OH) attached to the silicon atoms at the broken edges of the tetrahedral planes and (ii) exposed AlOH groups in layer silicates. The charge resulting from isomorphous substitution arises from the replacement of a silicon or aluminium atom by an atom of similar geometry but of lower charge (e.g. Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+}). This produces a net negative charge which is fairly uniformly distributed over the plate shaped clay particles. Negative charges also form at the edges of clay plates by reactions such as

$$-SiOH + OH^- \rightleftharpoons SiO^- + H_2O \qquad ....(4)$$

$$-AlOH + OH^- \rightleftharpoons AlO^- + H_2O \qquad ....(5)$$

The negative charge that develops on organic and mineral colloids is neutralized by cations attracted to the surfaces of these colloids. The quantity of cations expressed in milliequivalents is termed the

cation exchange capacity of the soil. It is one of the important chemical properties of soils and is usually closely related to soil fertility. Carboxyl and phenolic hydroxyl functional groups contribute most to the cation exchange capacity. This can be predicted from the analysis of titration data [7,8], from functional group analysis, infrared spectroscopy (in the case of carboxyls) and from the identification of products released from the degradation of the polymer [9]. Base saturation is another important property of a soil and generally reflects the extent of leaching and weathering of the soil. It is defined as the percentage of the total cation exchange capacity occupied by such basic cations as calcium, magnesium, sodium and potassium. Cation exchange capacity of a soil is not a fixed quantity but is dependent on the soil pH. Numerous studies have shown that the cation exchange capacity of soils is a continuous function of pH, with this value being lowest in the acid range, pH 3 to 4 and increasing continuously as the pH increases up to the alkaline range, pH 8 to 9. This increase in cation exchange capacity with increasing pH is caused by the ionization of the OH groups at the edges of the clay

lattice and on the hydrous Al or Fe oxides and from the carboxyl and phenolic groups present in soil organic matter. Contrary to cation exchange, the capacity for retaining anions increases with a decrease in soil pH. Further anion exchange is much greater in soils high in clays and those containing hydrous oxides of iron and aluminium. Anions may be retained by soil particles through a number of reactions, some of which are simply electrostatic [10] and are described as non specific. The positive charge sites responsible for electrostatic adsorption and exchange of anions originate in the broken bonds primarily in the alumina octahedral sheet, exposing OH groups on the edges of clay minerals.

A spectacular revolution began in 1935 with the discovery by two English Chemists, Adams and Holmes, that crushed phonograph records exhibit ion exchange properties. This led them to the synthesis of organic ion exchange resins [11], which consist of three dimensional networks of polymeric chains cross linked with short chains containing ionizable functional groups. Various improvements were made in the resins. A typical resin is prepared by polymerization of styrene and divinyl-benzene. The number of

cross-linkage is governed by divinylbenzene to styrene ratio. Organic ion exchange resins are stable towards acids. Their structure can be varied as desired. An increase in cross linkage increases rigidity, reduces swelling and the solubility of polymeric structure. Organic resins have been used in laboratories and industries for separations, recoveries of metals, purification of water, concentration of electrolytes and elucidation of the mechanism of many reactions. Several commercial resins, both cation (strong and weak acid) and anion (strong and weak base) exchangers are available for this purpose.

Cation exchange in soils is of great importance as it can alter the availability of several micronutrients [12]. In soils a number of cations may be present in trace quantities such as cobalt, copper etc., which are very beneficial to plants. A study of cation exchange in soils gives an idea about the capability of the soils to store [13] and supply [14] the nutrient elements to plants.

Adsorption at soil surface exerts the most profound influence of the several processes operating to determine the fate and behaviour of pesticides in

soil. It governs the relative availability of a pesticide, its volatilisation, physical distribution, breakdown, biological activity and even its susceptibility to microbial metabolism. It depends upon the nature and properties of the pesticide such as acidity, basicity, solubility, shape and configuration, charge distribution, polarity of molecule, molecular size and polarizability and its concentration in the solvent. The literature on this aspect has been reviewed by Bailey and White [15].

Several workers [16-33] have reported that the extent of pesticides on soils depends upon the clay content, organic matter content, cation exchange capacity, pH, moisture, exchangeable cations, temperature and other environmental conditions.

Organic matter is the most important of factors operating which determine the adsorption and fate of pesticide in soil. Stevenson [34] pointed out that information on the nature of organic matter-pesticide interactions may provide a more rational basis for their effective use, thereby reducing undesirable side effects due to carry-over and contamination of the environment. However, a proper

explanation of the precise nature of these interactions is hindered due to the complexity of organic matter and the numerous other interactions in the soil environment all operating simultaneously. In recent years careful studies with simplified systems involving well-defined organic matter components have resulted in the elucidation of some of the mechanisms of interactions. The merits of using organic matter components, such as humic acid and fulvic acid are (1) They can be readily extracted from soil organic matter in relatively pure form (2) They have been thoroughly characterized by various techniques and (3) They are the major and common constituents of soil organic matter.

A limitation that needs to be considered in adsorption of pests on soil surface is that in most mineral soils, organic matter and clay minerals are intimately associated in the form of clay-organic matter complexes. Thus, organic matter may not function as a separate entity and its relative contribution in pesticide adsorption will depend upon the extent to which the clay is coated with organic matter [34]. However, it should be realized that the

association of organic matter with clay still provides an organic surface for adsorption [34].

The texture and structure of soil also play a very important role in adsorption process. The soils having two layer clay mineral i.e. kaolinite, three layer clay minerals, montmorillonite, illite or hydrated aluminium and iron oxide surfaces of oxygen atoms or OH-groups are available for adsorption including hydrogen bonding. The clay are generally negatively charged and have exchangeable cations such as H^+, Na^+ and Ca^{2+} on their exterior surfaces (two layer minerals) or on their both exterior and interior surfaces (three layer minerals). Montmorillonite clays have higher surface area and cation exchange capacities followed by illite and kaolinite. All these clays strongly adsorb organic cations [35-37]. Clay minerals probably do not adsorb anions by anion-exchange, the layers of OH-groups of kaolinite are not exchangeable and number of edge OH-groups for kaolinite and montmorillonite is small. Hydrated Al and Fe-oxide associated with clay are probably responsible for adsorption of anions by anion - exchange.

Adsorption is of two types physical and chemical called as "physisorption" and "chemisorption" respectively. In the former the molecules are adsorbed to a solid surface by essentially the physical forces. In chemisorption, however, the molecule forms the chemical bonds with the solid surface. In case of physical adsorption there are vander waal's interactions (for instance dispersion or polar interaction) between the surface and the adsorbed molecule. These are weak types of interactions and the amount of energy released when a molecule is physisorbed is of the order of 25 kJ mol^{-1} i.e. the enthalpy of condensation. This energy can be adsorbed by the vibration of the lattice and is dissipated as heat. A molecule bouncing across the surface will loose its kinetic energy and stick to the surface resulting in the rise in temperature of the system, i.e. heat is evolved. In chemisorption which is shortening of chemical adsorption the molecules stick to the surface as a result of the formation of chemical bonds, usually covalent bonds and tend to find the sites that increase their coordination number

with the temperature. Thus the energy of attachment is greater than in that of physical sorption and is in the range of 40 KJ mol^{-1} to 200 KJ mol^{-1}. Sorption equilibria of Pb and Cu^{2+} has been discussed in our earlier studies [38,39]. For a spontaneous process chemisorption must be exothermic (barring the exceptional case). This can be explained as follows :

For a spontaneous process ΔG should be negative. As the species is adsorbed there is a reduction in its translational freedom so ΔS is also negative. Hence ΔH must be negative if $\Delta G = \Delta H + T\Delta S$ is to be negative and a negative ΔH value corresponds to the exothermic process. But sometimes the adsorbate dissociates at high temperature leading to breaking of bonds and thus has high translational mobility on the surface as in case of the adsorption of hydrogen on the glass surface, enthalpy is small and positive.

A formal distinction between the chemisorption and physiosorption was formerly the magnitude of the enthalpy of adsorbed ion. ΔH for physiosorption is rarely more negative than about -25 KJ mol^{-1} while that for chemisorption it is usually more negative and sometimes much more negative than -40 KJ mol^{-1}.

Plotting of adsorption isotherms is the most convenient way of studying and understanding the nature of adsorption taking place in a particular system. The isotherms are obtained by plotting the amount adsorbed against the equilibrium concentration at any instant at a particular temperature. Thus different types of curves with different slopes and initial portion of the curve are obtained. Based on these factors adsorption isotherms can be divided into four main classes and thereafter into subgroups. The main classes are as follows :

(a) Langmuir isotherm or L curves

(b) S. type of isotherms

(c) High affinity isotherm or H curves

(d) Constant partition or C curves.

Langmuir isotherms indicate that molecules are adsorbed flat on the surface or sometimes vertically oriented with strong intermolecular attraction. This is the best known isotherm. These curves occur in majority of cases of adsorption from dilute solution and for cases of the other types appear to have been previously recorded. The initial slope depends on the rate of change of site availa-

bility with increase in solute adsorbed. As more solute is taken up, there is usually progressively less chance that a bombarding solute molecule will find a suitable site on which it can be adsorbed. The initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find out a vacant site available. This implies that either the adsorbed solute molecule is not vertically oriented or there is no strong competition from the solvent. The types of systems which give this curve have one of the following characteristics.

(i) The adsorbed molecules are most likely to be adsorbed flat eg. resorcinol on alumina (ii) if adsorbed end on they encounter little solvent competition eg. high polar solute on substrate or systems with monofunctional ionic substances with strong intermolecular attraction.

S type curves indicate the vertical orientation of the adsorbed molecule at that surface. The initial part of the S curve shows that more solute is already adsorbed and it is easier for the additional amount to become fixed.

High affinity curves are given by solutes adsorbed as ionic micelles and by high affinity ions exchanging with low affinity ions. This is a special case of L curve in which the solute has such high affinity that in dilute solution it is completely adsorbed or at least there is measurable amount remaining in the solution. Thus the initial part is vertical. The adsorbed species are often large units i.e. ionic micelles or polymeric molecules, but sometimes they are apparently single ions which exchange with other ions of much lower affinity for the surface eg. sulfonated dye ions exchange with Cl^- alumina, cyanide dye on silver halide. In the most extreme cases the curve is a horizontal line running into the vertical axis.

And lastly the constant partition curves or the linear curves are obtained when the solute penetrates into the solid more readily than does the solvent. There is a constant distribution of solute between solution and substrate up to the maximum possible adsorption where an abrupt change to a horizontal plateau occurs. Such type of curves are obtained for the partition of a solute between two immiscible solvents. Favourable conditions for "C"

curve to appear are : (a) A porous substrate with flexible molecule and regions of differing degree of crystallinity and a solute with (b) higher affinity for the substrate than the solvent has and with (c) better penetrating power by virtue of conditions (d) and of molecular geometry, into the crystalline regions of the substrate.

The subgroups of these classes are arranged according to the shape of the parts of the curves farther from the origin, and the significance of plateau and changes of slope are described. Fundamentally, the linearity shows that the number of sites for adsorption remain constant i.e. as more solute is adsorbed more sites must be created. Such a situation arises when the solute has a higher attraction for the adsorbent than the solvent itself has. Thus the solute can break the inter substrate bond more readily than the solvent could, and if its molecular dimensions were suitable, it could penetrate to the structure of the substrate in regions not already penetrated by the solvent. This action has been compared to the opening of a zip fastener, the fastening represents the intermolecular bonds of the substrate, and the slider represents the first molecule or group of molecule of solute to penetrate.

This opens up the structure and allows more solute molecule to enter. This action stops abruptly when more highly crystalline regions of the substrate are reached. In fact the isotherms usually do suddenly change direction to give the horizontal plateau. Thus a linear isotherm indicates that the solute is penetrating the regions inaccessible to the solvent.

Nearly all sufficiently complete curves have either a plateau or an inflection(knee). Those that do not have plateau or knee are clearly incomplete i.e. surface saturation is not reached probably because of experimental difficulties. The plateau or the beginning of the linear portion above the "knee" must represent the "first degree saturation" of the surface i.e. the condition in which all possible sites in the original surface are filled and further the adsorption can take place only in new surface. For convenience this degree of coverage may be called the formation of a complete monolayer but this does not necessarily imply that it is a close packed layer of single molecule or ions, as in a compressed monolayer on water. It may be so in some cases and when it is specific surface area determination can readily be made. Generally however the layer may (a)

contain solvent as well as solute molecule or (b) consist only of isolated cluster of solute molecule adsorbed on the most active sites or (c) consists of ionic micelle either packed closely or well separated.

The significance of a long plateau must be that a high energy has to be overcome before additional adsorption can occur on new sites, after the surface has been saturated to the First degree. The solute has high affinity for the solvent but low affinity for the layer of solute molecule already adsorbed. Adsorption of ionic micelles give curves with long plateau. In this case the solid surface when covered will tend to repel other micelles holding the same charge. A short plateau means that the adsorbed solute molecule expose a surface which has nearly the same affinity for more solute as the original surface had.

Second rise or plateau are attributed to the development of a fresh surface on which adsorption can occur. The second plateau represents the complete saturation of the new surface.

The different models for adsorption applicable to both gases and liquids, are available in literature. They are however being discussed in brief as follows.

(1) **Langmuir Model**

Langmuir proposed

$$Ce/Am = 1/K \times 1/b + (1/b)\ Ce \qquad .....(6)$$

Where Ce is the equilibrium concentration and Am is the amount adsorbed per specified amount of adsorbent. K is the equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence a plot of Ce/Am Vs Ce should be a straight line, with a slope equal to 1/b and $\frac{1}{K} \cdot \frac{1}{b}$ as intercept.

(II) **Freundlich Model**

According to this model

$$Am = K\ Ce^{1/n} \qquad ....(7)$$

$$\ln Am = \ln K + 1/n\ \ln Ce \qquad ....(8)$$

Where all the terms have the usual significance and n is an empirical constant, thus a plot of ln Am Vs ln Ce should give a straight line with a slope equal to

1/n and intercept gives the value of lnK.

This model deals with the multilayer adsorption of the substance on the adsorbent.

Pollution is an undesirable change in the physical, chemical and biological characteristics of our air, water and soil that may or will harmfully affect human life, industrial progress, living conditions and cultural assets. Pollution is a man-made problem. Man-made pollutants not only damage environment, health, vegetation and materials, but also interfere with climate. Pollution involves an unhealthy mixture of foreign matter or energy into air, water and soil which makes it harmful to life activities. Air is easily polluted by gases, smoke, dust, etc., which are lighter objects and get mixed up in the atmosphere. Effluent from industry and human settlements have turned many great rivers and lakes murky. Dumping of industrial wastes containing poisonous chemicals has caused serious damage to agricultural lands and destruction of scenery. Effect of polluted irrigation water on crop plants show deleterious effects and decreases productivity. The grain quality is affected by heavy metals i.e. lead,

zinc etc. and pesticides which get accumulated in these. Soil provides us a place to live and is a reservoir of minerals but with accelerating growth of the world's population and rapid urbanisation tremendous pressure has been created on it.

Insecticides, Herbicides and other pesticides aiding agricultural development and health protection are very potent pollutants having long range effects and their indiscriminate use poses a serious danger to the structure and function of the ecosystems. To contain the menace of pollution it is necessary to educate people at all levels to conserve the environmental resources, and to find ways and means to effectively reduce the pollution hazards which are already existing. Man pollutes the environment by using it too much and then throwing off too much of the unused matter this brings an imbalance in the ecosystem.

With the emerging new Science and technology there has been improvement in the quality of life and its expectancy. With the ever increasing trend in the world population, problems of food, health and hygiene are widening day by day [40] and putting

pressure on man to increase agricultural production which has led to greater exploitation of land, frequent use of pesticides and other agro chemicals. When soils come in contact with pesticides their physico-chemical and biotic properties are affected. The indiscriminate use of pesticides can pose a serious danger both to the human health and the environment [41]. Pesticides while eliminating the beneficial insects may cause ecological imbalance. At the same time they are phytotoxic and destroy useful plants. They enter the food chain causing toxicity to human beings, animals and other creatures. Quite a large amount of pesticides reaches the water resources causing toxicity to flora and fauna. By and large, pesticides are toxic chemical substances which are used to kill pests of widely different taxonomic categories. The pesticides are commonly characterized on the basis of target group of organisms such as fungicides against fungus, insecticides against insects, herbicides against herbs, nematicides against nematodes etc. Roughly one third of the crops are lost due to insects, pests, weeds and other diseases. On an average, farmers lose between 40 to 50 percent of their crops before harvest. Although, the turn of the present century

would see an enormous increase in food production, particularly in the developing countries, still the Food and Agricultural Organisation of United Nations foresee that by the year 2000 A.D. there will be scarcity of food especially in Africa, Latin America and parts of Asia. This brings into sharp focus the dire need for plant protection. The use of pesticides is expected to increase immensely as the crops would need an effective plant protection umbrella in the time to come.

This chemical crop protection is nothing but a profit induced poisoning of the environment. Many books [42-47] and reviews [48-50] have been published and symposia organised on the subject as a warning of the potential hazards. According to the World Health Organisation report every minute someone is poisoned by pesticides in the developing countries. A pesticide caused death occurs every one hour and 45 minutes in the third world countries. Consequently there is a growing concern about the use of pesticides throughout the world. A matter of serious thought is the fact that about half of the pesticide poisoning cases leading to death are from the third

world countries although these account for only 15 percent of the total consumption of pesticides. This is a pointer towards indiscriminate use and lack of awareness about the hazardous side effects of pesticides.

Generally pesticides are classified into two broad categories namely -

(i) Inorganic Pesticides

(ii) Organic Pesticides

<u>Inorganic Pesticides</u> : Several, inorganic compounds containing aresenic, lead, copper, antimony, boron, and zinc are known as inorganic pesticides. Some of the examples of well known inorganic pesticides are (I) arsenic compounds such as paris green[$(CH_3COO)_2Cu.3Cu(AsO_2)_2$], basic copper arsenate [Cu ($CuO \cdot HAsO_4$] (ii) fluorine compounds such as calcium fluosilicate ($CaSiF_6.2H_2O$) (iii) Mercury compounds such as mercuric chloride ($HgCl_2$) (iv) boron compounds such as borax ($Na_2B_4O_7$).

The use of inorganic pesticides [44] to kill pests is not a new concept. These inorganic pesticides are known to cause several harmful effects. Arsenical

poisons and boron causes mutations in the reproductive parts of the plants causing semi-permanent sterility while copper ions react with enzymes having reactive sulphydryl groups, which explains their toxicity to all forms of plant life. Many enzymes containing iron, calcium, magnesium are inhibited by fluoride ions. Accumulation of lead in the body causes coagulation of body protein disrupting seriously the metabolic activities, it is also mutagenic when accumulated in the body tissues, mercury causes blurred vision, severe illnesses, headache and abnormalities not only in the person exposed but also in the next generation to come. Zinc accumulation results in the disintegration of liver, kidneys and heart.

Organic Pesticides : The era of organic pesticides began in 1939 [51] when the first wonder pesticide Dichlorodiphenyl trichloroethane (DDT) was discovered, although it was synthesised in 1874 by Zeidler. Its insecticidal properties were discovered by Muellar in 1939 for which he was awarded the Nobel Prize. This was soon followed by Benzenehexachloride (BHC). Since than thousands of compounds have been synthesized and

tested for their pesticidal properties. More than 1200 pesticides were registered by the United States Environmental Protection Agency (USEPA) [52]. Of these, 275 were herbicides, 400 were insecticides, 200 were fungicides and nematicides, 100 were rodenticides and 275 were disinfectants, all being sold in the form of 30,000 or so products or formulations.

Organic Pesticides have been classified as:

(a) Organohalogenated Pesticides.
(b) Organophosphorus & Sulphur containing pesticides.
(c) Organocarbamate pesticides.
(d) Pyrethroids.
(e) Miscellaneous Pesticides.

<u>Organohalogenated Pesticides</u> : Several organohalogenated pesticides such as Aldrin, DDT, BHC, Endosulphan etc. are used for crop protection. These pesticides belong to the following sub-groups (I) Diphenyl aliphatics having an aliphatic or straight carbon chain with two diphenyl rings attached e.g. DDT, DDD chlorobenzilate, dicofol, perthane. (II)

Chlorinated benzene ring structure e.g. BHC and lindane (III) Cyclodienes having three dimensional structure with active stereoisomers e.g. aldrin, dieldrin, endosulphan and heptachlor(IV) polychloro-terpenes e.g. strobane and toxaphene.

These pesticides are toxic to insects and other arthopods at very low dose. The cost is low because of their high persistency. Few annual treatments are necessary to maintain pest at low levels. These compounds tend to accumulate in food chains. These compounds are well soluble in organic solvents including fat but are poorly soluble in water.

Organophosphorus and Sulphur containing pesticides:

These pesticides have a wide range of toxicity. They are known to inhibit the activity of the enzyme, acetylcholinesterase. During the course of their action they result in excessive sweating, headache, giddiness, blurred vision and muscular weakness. They also bring about destruction of mylin sheaths of sciatic and spinal nerves. High dosage leads to rapid paralysis and possible death.

Organocarbamate Pesticides : Carbamate belong to a new and comparatively small group of pesticides of growing utility. They bridge the gap between the persistent organochlorine and the short lived but excessively toxic organophosphorus pesticides. This group includes highly effective systemic pesticides such as aldicarb, baygon, carbaryl, carbofuran, lannate and oxamyl. The mode of action of carbamate is similar to that of organophosphorus pesticides.

Pyrethroids : The first synthetic pyrethroid was described in 1973 and many new photostable pyrethroids were synthesized between 1973-1977. These compounds exhibit high activity against insects, low mammalian toxicity, greatly increased stability effectiveness at very low dosages, rapid action and degradation to innocuous residues. These compounds are more effective as contact pesticides and a lesser extent as stomach poisons. The following compounds are registered to be marketed in India - Permethrin, Cypermethrin, Decamethrin and Fenvalerate.

Miscellaneous Pesticides : Since search and synthesis of new pesticides has always been in consideration

and with time more and more pesticides are being listed which do not fall in any of the above categories. To cite a few are formamidines, amitraz and chlorodimeform, thiocyanates, lethane 384 and thanite dinitrophenol dinocap, organotins, pyrethrins, rotenones and triazines. These compounds also have slow deletrious effect on the health of the crops, soil organisms and human beings. When these compounds are applied to soil or to standing crops, they are adsorbed and move to a certain depth in soil depending upon various soil properties and may pollute the sub-soil water.

Pesticides are introduced into the soil for destroying soil-dwelling pests, nematodes and the pathogens of bacterial and fungal diseases. Pesticides also get into the soil after treatment of the green organs of plants : they are washed off by atmospheric precipitation and carried off by the wind. The property of pesticides to withstand the decomposing action of physical, chemical and biological (biochemical and microbiological) processes characterize their persistence. Depending on the conditions, poisonous chemicals may remain in the soil unchanged and retain their toxicity for a

more or less prolonged period. The persistence of various compounds when studied in the same conditions (or of the same compound but in different soils) is characterized by the parameter $t_{1/2}$ (the half life) which denotes the time during which the content of the relevant pesticide in the soil is halved in comparison with the original amount.

The persistence of pesticides in the soil depends on their chemical and physical properties, the dose, formulation (powder, liquid etc.) the type of soil, its moisture content, temperature and physical properties, the composition of the soil microflora, the specific composition of the growing plants and the features of soil tilling. Pesticides incorporated into the soil in the form of granules persist in it for a longer time than powders or liquid substances. Pesticides as a rule are more persistent in soils with a high content of organic matter and a silt fraction. Pesticides and their metabolites are found in the soil in a labile state with all three of its phases and can therefore migrate along the soil profile in a horizontal and vertical directions. Poisonous chemicals move in the soils owing to molecular diffusion with the capillary

moisture, the descending flow of gravitational water, the root system of plants and as a result of displacement when the soil is being tilled. Pesticides travel over large distances with the stream of water appearing after rainfall or irrigation. The rate and depth of vertical movement depend on the solubility and dose of the pesticide, the features of its adsorption and desorption, its volatility (vapour pressure), and also on the intensity of evaporation of the soil moisture.

Pesticides become modified or completely decomposed in the soil as a result of physicochemical processes, microbiological decomposition and the sorption by higher plants and the soil fauna. Many pesticides become detoxicated owing to their adsorption by humus and other colloids or to the formation of stable complexes in the soil. Poisonous chemicals are removed from the soil as a result of volatilization, evaporation with water vapour, migration beyond the root habitat layer, washing out by rain water, melted snow, irrigation, ground and soil water.

Pesticides incorporated into the soil lose a part of their activity because of their being

adsorbed by the soil colloids. The degree of adsorption of most pesticides largely depends on the humus content in the soil. In the adsorption of pesticides the adsorption surface of the soil and the degree of its affinity to a given pesticide (the magnitude of the surface energy) are of major importance. Adsorption of some pesticides may also depend on the pH, pK and hydrolytic acidity of the soil. The degree of adsorption of pesticides depends not so much on the content of the clay and silt particles in the soil as on the nature and origin of the clay minerals that are distinguished by the magnitude of the surface of the particles and the structure of their crystal lattice. Consequently, the nature of adsorption of a pesticide will vary depending on whether an anion or a cation is the active part of a pesticide molecule or whether its molecule is ampholytic or electrically neutral and does not dissociates. The degree of adsorption of pesticides by the soil depends greatly on its moisture content. The larger the amount of water sorbed by the colloids, smaller is the free space remaining for the adsorption of pesticides. The nature of adsorption also depends on the chemical structure of the pesticide, its basicity and on the properties of its functional groups to form hydrogen

and dipole bonds. The adsorption of pesticides in the soil also depends on its temperature. This is of a practical significance because triazine incorporated into the soil in cold and damp weather are adsorbed in the top layer of the soil, which prevents their being washed out or decomposed. Becoming desorbed when the weather gets warmer, they again exhibit their activity. Precipitation and elevation of temperature facilitates the desorption of pesticides sorbed by the soil. Evaporation with water vapour is one of the factors leading to the loss of toxicity in the soil of insecticides such as heptachlor. Pesticides may also decompose in the soil under the influence of elevated temperatures. The hydrolytic and oxidation transformations of many pesticides in the soil appreciably lowers their toxic action.

An important role is also played by the chemical structure of the pesticide and its properties. The kind and number of halogen atoms and their arrangement in a molecule affects the rate of decomposition of halogenated pesticides and their derivatives. The length of the hydrocarbon chain in aliphatic acids also affects the persistence of such

pesticides. The decomposition of most pesticides in the soil is associated with microbiological activity through reactions such as dehalogenation, dealkylation, amide or ether hydrolysis, oxidation, reduction breaking of an ether bond, hydroxylation of an aromatic ring and breaking thereof. The nature of decomposition also depends on the features of the enzyme produced by the microorganisms. Several enzymes produced by various microorganisms are responsible for decomposition at definite stages. As a rule aromatic substances with a cyclic structure decompose considerably with more difficulty than compounds of the fatty series. Dehalogenation consists in the detachment of halogen atom from a pesticide molecule. Of major significance for the dehalogenation of pesticides is the number, position and kind of halogen atoms in the compound. An increase in the number of halogen atoms in a pesticide molecule and also an increase in the distance from the functional group lowers the rate of decomposition reaction. This is why a compound in paraposition is decomposed more readily than when it is in metaposition. Dealkylation of pesticides in the soil may take place with breaking of the bond C-R, N-R or O-R. Oxidation of pesticides in the soil by microorganisms proceeds

diversely, relatively stable organochlorine compounds having a double bond may be oxidized to epoxides. Organochlorine insecticides as a rule are the most resistant to microbiological decomposition in comparison with other derivatives but microorganism oxidise heptachlor to neptachlor epoxide. The accumulation of persistent pesticides in the soil in a number of cases leads to their translocation into the stems, leaves and root vegetables. The level of the content of a pesticide in a plant is determined by sorption, the supply and decomposition of the toxicant in the plant and the soil. As a whole the intensity of migration of a pesticide from the soil into a plant and its accumulation in the productive organs depend on its content in the soil, although there is not always a direct relation between these parameters.

Pesticides incorporated into the soil may change the composition of the soil microflora. Organochlorine insecticides in the doses recommended for controlling soil-inhabiting pests do not have a negative influence on the number of soil microorganisms. Rapidly decomposing organophosphorus insecticide in the recommended doses stimulate the development of separate groups of microorganisms and

in increased doses first cause suppression and then stimulation of the soil microflora. Soil fungicides and fumigants as a rule, have a negative effect on the soil microflora. The biological activity of the soil or the intensity of soil respiration (the absorption of O_2 and the evolution of CO_2) may be used as a general parameter showing how pesticides act on the soil microflora. The change in the activity of the soil enzymes in definite conditions characterises the effect of pesticides on the microbiological activity in the soil. The effect of pesticides on biological processes in the soil comes to light the most clearly only upon a repeated or multifold application of the toxicants. The nature and degree of action of pesticides on soil fauna are due to the properties of the substances, their content in the soil the composition of the fauna and to the soil and climatic conditions. In some cases, pesticides stimulate the reproduction of the soil fauna, in others they cause its suppression and extermination. Unstable rapidly decomposing pesticides are less dangerous to the soil fauna. Persistent compounds upon their surplus accumulation are a great danger. Organochlorine insecticides such

as heptachlor and toxaphene in their usually recommended doses act weakly on or are completely harmless to earthworms and nematodes but are toxic to soil arthropods.

Several mechanisms have been reported for adsorption of pesticides on soil such as Vander Waal's attractions, Hydrogen bonding, Hydrophobic bonding, charge transfer, ion exchange and ligand exchange.

Vander Waal's Attraction :

Vander Waal's forces are involved in the adsorption of nonionic, nonpolar molecules or portions of molecules. Vander Waal's forces result from short range dipole-dipole interactions of several kinds. The additive nature of Vander Waal's forces between the adsorbate and adsorbent may result in considerable attraction for large molecules. The adsorption of carbaryl and parathion on soil organic matter in aqueous system is considered to be physiosorption involving Vander Waal's bonds between the hydrophobic portions of the adsorbate molecules and the adsorbent surface . Nearpass [53] suggested that the principal adsorption mechanism for

picloram by humic materials was molecular adsorption due to Vander Waal's forces. Singh et al. [54] found that adsorption of dimethoate decreased with the rise of temperature indicating the involvement of Vander Waal's forces during adsorption process.

Hydrogen Bonding : This is a special kind of dipole-dipole interaction in which the hydrogen atoms serve as a bridge between two electronegative atoms, one being held by covalent bond and the other by electrostatic forces. There is a difference between hydrogen bonding and protonation [55]. Protonation may be considered as a full charge transfer from the base to the acid while hydrogen bonding interaction is a partial charge transfer interaction [56]. Erik et al. [16] suggested that H-bonding was considered the most feasible adsorption mechanism of lindane. Hayes [57] stressed the participation of a hydrogen bonding mechanism in S-triazines and organic matter interactions. Borggard and Streibig [58] have suggested hydrogen bonding as an adsorption mechanism in atrazine adsorption by soils.

Hydrophobic Bonding : Nonpolar pesticides are likely to adsorb onto the hydrophobic regions of the soil.

Water molecules present in the system will not compete with nonpolar molecules for adsorption on hydrophobic surfaces. This type of bonding may be largely responsible for the strong adsorption by soil organic matter of organochlorine pesticides. Lipids are also associated with soil humus [59].

Thus association of nonpolar (chlorinated hydrocarbons) pesticides with the lipid fraction of soil organic matter and humus might be described by hydrophobic bonding [60]. This also explains the relative independence of pesticide adsorption on moisture in soils with high organic content [60]. The adsorption of pesticides involving this mechanism would be independent of pH [61]. Methylation of organic matter or humic substances to block hydrophilic OH groups would increase the adsorption by this mechanism. Kozak et al. [62] also suggested hydrophobic bonding as a possible explanation in prometryn and metolachlor adsorption.

Charge Transfer : Charge transfer interaction will take place only within short distances of separation between the interacting species. In the formation of charge transfer complexes, elecrostatic attraction

takes place when electrons are transferred from an electron rich donor to an electron deficient acceptor. Burns et al. [63] postulated the involvement of charge transfer mechanisms in paraquat adsorption by humic acid.

Ion Exchange : Ion exchange adsorption takes place for those pesticides which either exist as cations or which become positively charged through protonation. Adsorption of pesticides, such as paraquat and diquat, via cation exchange functions through -COOH and phenolic-OH groups associated with the soil organic matter [64]. Bansal [22] also suggested this type of mechanism in the adsorption of oxamyl and dimecron by some soils. The cationic adsorption mechanism is also responsible for the adsorption on organic matter of less basic pesticides, such as S-triazines [65].

Ligand Exchange : Adsorption by this mechanism involves replacement of one or more ligands by the adsorbent molecule [66, 67]. The necessary condition is that the adsorbent molecule be a stronger chelating agent than the replaced ligands [68].

This type of mechanism may be involved for the binding of S-triazines on the residual transition metals of humic acid [69].

In ligand exchange partially chelated transition metals may serve as possible sites for adsorption [57]. Coordination through an attached metal ion, ligand exchange was considered to be the main process in the adsorption of linuron by peat samples saturated with different cations [70].

The chemical and physical properties of soils are influenced strongly by soil constituents which have high surface area and surface density of charge. The colloidal fraction of the soil, is thus the dominant factor in influencing interactions between pesticide molecules and the soil. The colloidal components of soil may be divided into the mineral fraction and organic fraction.

Factors influencing the adsorption of pesticides by Soil Colloids

(1) Physico-chemical character of the adsorbent: The properties of the adsorbent which influence its behaviour in interactions with the adsorbate are

primarily related to the area and configuration of the surface and to the magnitude distribution and intensity of the electrical field at the surface. The manner in which the surface charge density can be of importance in understanding the adsorption of pesticides has been illustrated in a very elegant manner by Weed and Weber [71]. The compounds used in this study were diquat and paraquat. Paraquat charges are about 7A° apart whereas the diquat charge centres are 3.5A° apart. It was observed that at low surface charge densities paraquat was preferentially adsorbed over diquat. With increase in surface charge density the adsorption sites are more closely spaced and diquat was preferentially adsorbed due to the shorter separation of its charge centres (3.5A°).

The adsorbent may influence adsorption through its effect on the orientation of the adsorbate. Information in this aspect has been primarily derived from x-ray diffraction studies. Green-Kelley [72]. found that saturated and unsaturated ring compounds formed two main types of complexes, depending upon whether the rings lie parallel to d_{001} of montmorillonite or perpendicular to d_{001}.

(2) Physico-chemical character of the adsorbate :

Examination of a pesticide's structure and physico-chemical properties often permits estimation of its adsorption behaviour. These include (a) overall chemical character, shape and configuration (b) acidity or basicity (c) solubility (d) electronic effects (charge distribution, polarity and polarizability) and (e) molecular size [73]. These factors are of help in isolating the important pesticide characteristics affecting adsorption. The chemical character is largely determined by the number, nature and relative position of functional groups. Adsorption is characteristically increased with functional goups such as R_3N^+-, $CONH_3$, -OH, -NHCOR, $-NH_2$ and NHR. Several workers have attempted to corelate molecular structure and adsorption to soil. In a study [73] on the effect of functional group, nature and position of ring substitution on the magnitude of adsorption of a wide variety of compounds, concluded that the chemical character of the molecule affects retention by colloidal systems in three different ways : (1) determines if the molecule is fundamentally acidic or basic in nature and the relative acidic or basic strength (2) affects the

water solubility of the molecule and (3) determines the relative importance to (1) and (2) of Vander Waal's type forces. A fundamental relationship [73] between adsorption by soils and chemical structure of certain classes of chemicals has been mathematically derived. This relationship is based on extra-thermodynamic linear free energy approximations.

(3) Soil Reaction : The importance of soil pH as a factor affecting pesticide adsorption depends largely on the pesticide itself. pH is manifested in determining the degree of dissociation or association of the compound, that is whether the compound is still a molecule or has dissociated into either a cation or anion. This in turn may affect the amount that is adsorbed and the strength with which it is held, since the energy of adsorption may be vastly different between the dissociated and associated form. Adsorption of herbicides with different molecular structures generally increases as pH decreases. The pH where maximum adsorption occurs is a function of the particular compound and the adsorbent. Herbicides are adsorbed in highest amounts at pH levels in the vicinity of their respective pK values. For instance, maximum adsorption of promethone

(pKa 4.28) occurs in the range of pH 4.2 to 5.2 addition of HCl or NaOH to lower or raise the pH results in decreased adsorption.

(4) Effect of temperature : Increased temperature, in general, leads to decreased adsorption as physical adsorption is characteristically an exothermic process. This corresponds to a weakening of attractive forces between the solute and the solid surface with increasing temperature and corresponding increase in solubility of the solute in the solvent. In a study of the adsorption of chloropicrin by soil it was found that lowering of temperature resulted in increased adsorption but this increase was completely recovered by bringing the samples back to the original temperature. Since desorption is interrelated with bioactivity, the bioactivity of pesticide might be expected to be different at various temperatures.

(5) Effect of salts : Soils generally contain inorganic salts such as sodium chloride or magnesium sulphate which may influence the adsorption equilibrium. It appears that at normal pH's dilute

salts slightly increase adsorption while concentrated solutions sharply increase adsorption. Work on the effect of salts on anionic materials has not been reported.

The cosolvent theory was proposed to describe sorption of hydrophobic organic compounds to soils from water/miscible solvent mixtures [74] . It has been applied to the sorption of several organic compounds of moderate and intermediate hydrophobicity. [75, 76]. The theory predicts a log-linear relationship between the mole-based equilibrium sorption partition coefficient (Km) and volume fraction solvent (fs). In its simplest form, the theory can be expressed as

$$\log (K_{mi}/K_{mw}) = -\alpha\sigma_s fs \qquad ....(9)$$

where K_{mi} and K_{mw} are mole-based partition coefficients (mol/g) for water/solvent mixture i and solvent free water, respectively. The term σ_s in equation 9 reflects solute-liquid interactions in that it is the slope of the log-linear relationship between mole fraction solubility and fs [77].

The term α in equation 9 is related to solute-soil and solvent-soil interactions via liquid and organic carbon phase activity coefficients [74,76].

The cosolvent theory is important for two reasons. First the theory enables prediction of sorption of an organic solute from a specified mixture of water and miscible organic solvent. This has implications on understanding fate and transport of organic contaminants in real-world, complex waste streams such as industrial wastes and landfill leachates. Second, the theory can be utilized to estimate K_D (Partition coefficient) for sorption from aqueous solution by log-linear extrapolation of K_{Di} data generated at higher fs, where K_{Di} is the volume-based sorption partition coefficient (mL/g) corresponding to liquid phase i, and is related to K_{mi} by the expression

$$K_{mi} = K_{Di}/V \qquad \ldots\ldots (10)$$

where V is the molar volume of the liquid phase (mL/mol). This is particularly significant for highly hydrophobic compounds because direct experimental determinations of sorption from water are extremely difficult to make.

Helling and Turner [78 - 80] introduced Soil Thin layer chromatography technique as an

alternate procedure for rapid reproducible and simple assessment of pesticide movement in soil. Some progress has been made in this technique in detail by autoradiography. Singh et al.[81-83], Sharma et al. [84 - 87] have studied the movement of certain pesticides on soil TLC plates and the movement was expressed in terms of R_f values which is measured using the following relation.

$$R_f = \left(\frac{R_L + R_T}{2}\right) \qquad \ldots(11)$$

Where R_L and R_T denotes the R_f of the leading and trailing regions respectively.

Thermodynamics is an appropriate means of describing the theoretical behaviour of sorption/ ion exchange equilibria. Equilibria can be described in general by means of rigorous thermodynamics. This requires no model and no assumptions about the mechanism of sorption/ion exchange phenomena. However, rigorous thermodynamic treatment gives a minimum of information about the physical causes of the phenomena; therefore its practical utility is restricted. An interpretation in terms of the underlying physical forces requires a model. The

properties of any particular model are reflected in form of the equations obtained and usually also in the physical interpretation to which these equations lead. This suggests that there are a number of different theoretical approaches. Two most appropriate theoretical approaches are usually applied for this purpose.

In the first approach more and more elaborate models are designed for deriving equations which reflect the action of various physical forces. These models have particular properties resembling those of ion exchangers. This approach gives a semiquantitative picture to understand the physical causes of the phenomena.

In the second approach various attempts have been made to correlate the activities, with some measurable quantities; the thermodynamic equations. The earliest approaches were based on semiemperical or emperical equations to fit the experimental results. Probably the first quantitative formulation of sorption/ion exchange equilibria was made by Gans [88]. For this purpose he used the law of mass action in its simplest form, without involving the

concept of activity coefficient. This concept was accounted for by Kielland [90]. Gaines and Thomas [89] gave a general treatment using an expression for the calculation of thermodynamic equilibrium constant which is a suitable choice for this purpose.

The thermodynamic equilibrium constant (K_o) for sorption on soils can be calculated by Biggar and Cheung method [19] where

$$K_o = \frac{C_s}{C_e} \cdot \frac{\nu_s}{\nu_e} \qquad \ldots\ldots(12)$$

where C_s is the amount of solute per gram of the solvent in contact with the soil or exchanger phase, C_e the concentration of the solute in solution phase, ν_s the activity coefficient of solute in soil and ν_e the activity coefficient of solute in solution phase. From the value of thermodynamic equilibrium constant, free energy changes (ΔG°) during the sorption/ion exchange phenomena can be calculated from the relationship

$$\Delta G^\circ = - RT\ln Ko \qquad \ldots\ldots(13)$$

where R is universal gas constant and T the absolute temperature.

The enthalpy change of the system can be calculated by using the integrated form of the Van't Hoff equation

$$\ln \left(\frac{K_{T_2}}{K_{T_1}}\right) = - \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad ..(14)$$

The change in enthalpy predicts whether the reaction is endothermic or exothermic. Enthalpy change of the system is directly related to changes in the number and strength of the bonds in the ion exchange process. The randomness of the ion exchange process may be predicted from the values of the free energy and enthalpy changes. The entropy changes can be calculated from ΔH° and ΔG° values using the equation -

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad ....(15)$$

at a given temperature, the overall entropy of the system reflects the extent of order produced during the ion exchange process.

In the present work sorption equilibria of cobalt(II) was studied on Indian soils - the natural ion exchangers with the purpose of understanding the basic chemistry of cobalt(II) in soils and to evaluate thermodynamic parameters for its interaction with the soils.

Sorption equilibria of pesticide, endosulphan was studied on Indian soils - the natural ion exchangers under the influence of organic solvents methanol and acetone by creating an adsorption system consisting of a liquid phase water with an organic solvent, soil and the pesticide. The applicability of the co-solvent theory was also evaluated. The effect of different factors such as exchangeable cations (H^+ and Na^+) organic matter, surfactants (non-ionic and anionic) and temperature on the sorption equilibria of pesticide, endosulphan; on soils was also studied. Thermodynamic parameters were evaluated for the interaction of endosulphan with soils. These studies will be helpful towards assessing endosulphan movement in soil and controlling soil pollution.

Movement of different pesticides in soil has been studied using thin layer chromatographic technique. The data obtained will be helpful in examining the probability of pollution of groundwater by the pesticides.

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CHAPTER II

SORPTION EQUILIBRIA OF COBALT(II) ON TWO TYPES OF INDIAN SOILS - THE NATURAL ION EXCHANGERS

II.1 INTRODUCTION

Since the earliest use of fertilizers containing micronutrients there has been an increasing interest in fixation of heavy metal ions by soils. The adsorption of metal cations by soils has importance in determining their availability to the plants and their movement through soils.

Cobalt is retained in soils by ion exchange/ adsorption and its deficiency or excess may cause problems in green plants. Cobalt is required by legumes such as soyabeans and alfalfa for the fixation of elemental nitrogen by Rhizobia [1]. The essentiality of cobalt is due to the part it plays in the formation of Vitamin B_{12} cyanocobalamine which in turn is essential for the formation of haemoglobin, whose concentration in the nodules is directly related to the nitrogen fixation by legume bacteria [2,3]. Cobalt deficient legumes develop the symptoms of nitrogen deficient plants [4]. Cobalt is also responsible for the quality of the fruit [5] and yield such as in mango plants. From the standpoint of the practical production of legumes cobalt is considered very essential [2].

Kevin G. Tiller et al. [6] have studied the specific sorption of cobalt by soil clays. Aly abd-Elfattah and Koji Wada [7] have also studied adsorption of cobalt by soils that differ in cation exchange materials. More recently Cai Zucong and Liu Zheng [8] have studied the determination of cobalt in soils. The purpose of this investigation was to study the sorption equilibria of cobalt(II) on soils; the natural ion exchangers at different temperatures, to understand the basic chemistry of cobalt(II) in soils and to evaluate thermodynamic parameters for the interaction of this metal with the soils.

II.2 EXPERIMENTAL

II.2.1 Reagents : Cobalt(II) nitrate [$Co(NO_3)_2.6H_2O$] B.D.H. was used. All other chemicals used were of Analytical Reagent grade.

II.2.2 Apparatus : An electric temperature controlled SICO shaker was used for shaking; an Elico pH meter model Li-10 for pH measurements; a systronic conductivity meter dip type cell for electrical conductance measurement and Bausch and Lomb spectrophotometer model spectronic 20 for the determination of cobalt(II).

II.2.3 Collection of Soil Samples : The soils used in the present investigation were surface samples (depth 0-30 cm) obtained from Tehri (Uttar Pradesh) and Bhopal (Madhya Pradesh). Both the soils were grounded in a hammer mill fitted with a sieve to obtain samples with a small and nearly homogeneous particle size.

II.2.4 Cation Exchange Capacity : The cation exchange capacity of the soil was determined by Ganguli's method [9]. In this method a 10 gm sample of the air dried soil was treated with 0.2N HCl till acidic,

shaken for half an hour and than filtered through Buchner funnel till the filtrate was free from chloride ions. The residue was transferred from the Buchner funnel to a beaker and a suspension of known concentration was prepared. It was then treated with the same volume of a saturated KCl solution, shaken for half an hour and left overnight. The exchanged acidity was titrated with standard 0.1N NaOH solution using phenolpthalein as an indicator. From the amount of NaOH required, the cation exchange capacity of the soil was calculated.

II.2.5 pH and Electrical Conductance : For this purpose a 1:2.5 soil–water suspension was prepared by adding 10 gm soil sample to 25 ml distilled water in a stoppered conical flask. The suspension was kept overnight and pH of the supernatant liquid was measured at 25°C. The electrical conductance of the soil water suspension was measured with a systronic conductivity meter dip type cell [10].

II.2.6 Percentage of Organic Matter : The organic matter content of the soil was determined by the method proposed by Walkley and Black [11]. For this

purpose, 2 gm of air dried, crushed and sieved soil was taken in a 500 ml conical flask. To this flask, 10 ml of 1.0 N potassium dichromate and 20 ml of concentrated sulphuric acid were added. The flask was shaken vigorously and allowed to cool for 30 minutes. Thereafter, 200 ml of distilled water, 10 ml of phosphoric acid and 1 ml of diphenylamine indicator were added to it. The amount of unreacted potassium dichromate was titrated with 0.5 N ferrous ammonium sulphate solution till the violet colour changes to purple and finally to green. Reagent blank determination was also carried out in the same manner. The percentage organic matter was then calculated by the equation

$$\% \text{ Organic matter} = \frac{(x-y)\ 0.003 \times 100}{2 \times \text{Weight of the soil}} \times 1.724 \quad ..(1)$$

where x and y are the volume (ml) of 0.5 N ferrous ammonium sulphate solution required for blank and sample solution respectively. To calculate the percentage of organic carbon in soil divide the value obtained for organic matter by the factor 1.724.

II.2.7 Surface Area : The surface area of the soil sample was determined by the method proposed by Dyal and Hendricks [12]. For this purpose, 2 gm of the soil sample was taken in a small aluminium box and placed in a vacuum desiccator over 250 gms P_2O_5. The weight of the dried sample was measured. The sample was then wetted with ethylene glycol added from a pipette dropwise and placed in a vacuum desiccator at room temperature to evaporate excess of ethylene glycol. The sample was weighed several times till a constant weight was observed for two successive weighings. Surface area was then calculated from the equation

$$\text{Surface Area} = \frac{W_2 - W_1}{W_1 \times 0.00031} \qquad \ldots\ (2)$$

where W_1 and W_2 are weight (in grams) of the dried sample and sample wetted with ethylene glycol respectively and 0.00031 is the Dyal and Hendricks value for the grams of ethylene glycol required to form a monolayer of one m^2 of surface area of the soil.

II.2.8 Calcium Carbonate Content : The calcium carbonate content of the soil was determined by

taking 10 gms of each of the sample on a Buchner funnel. The sample was washed with distilled water till free from chloride ions. It was then transferred to a conical flask, treated with 50 ml of 1.0N HCl solution, shaken and boiled on a steam bath till the reaction was over. It was than cooled to room temperature and back titrated with 1N NaOH using phenolphthalein as an indicator. The end point was recorded when the pink colour persisted for 15 seconds on shaking the solutions.

II.2.9. Mechanical Composition of Soil - Percentage of Sand, Silt and Clay : The mechanical analysis of soil was carried out by International pipette method [13]. A 10 gm soil sample was weighed and placed in an evaporating dish. Add 10 ml of H_2O_2 mixture warmed upto 60°C and stirred till no further evolution of gases occurred. The excess of H_2O_2 was decomposed by boiling for few minutes. After cooling, 10 ml or more 0.2 M HCl was added till the solution becomes acidic. It is then filtered and washed with warm distilled water till the washings showed no indication of acidic nature. The precipitate was transferred to an evaporating dish, 10 ml of

distilled water and 50 ml of sodium oxalate solution (8 gm/l) were added. The mixture was warmed and shaken by a high speed stirrer for about 15 minutes, 150 ml of distilled water was then added and the suspension washed through 200 B.S. sieve using not more than 150 ml of distilled water. The suspension which passed through the sieve was transferred to a graduated boiling tube or 500 ml measuring cylinder and volume was made upto 500 ml with distilled water. The residue on the sieve was dried and weighed. The dry sand is again passed through 25, 72 and 200 mesh size sieves and each fraction retained on the sieves is weighed in a watch glass which gives the coarse, medium and fine sands (Wcs, Wms and Wfs).

The 500 ml suspension was immersed in a constant temperature water bath at 25°C for one hour. The tube was then taken out, shaken up and down vigorously and is put back in the bath, simultaneously a stop watch is started. After a sedimentation time of 4 minutes 8 seconds, a 10 ml suspension from a depth of 10 cm is taken out by means of a sampling pipette and is transferred to weighed petri dish, dry it in an oven and weigh it. Repeat this procedure after 46 minutes and 6 hours 54

minutes and after commencement of sedimentation the boiling tube being shaken afresh in both cases. In each of the above case the weight of the solid material in 500 ml of the suspension was determined. The method of sampling is important, the pipette should be lowered into the suspension at a slow rate in order to avoid disturbance. The percentages of silt and clay were then calculated from the weights of the residues.

II.2.10 Adsorption Studies : For adsorption studies 1 gm soil sample was taken in different stoppered conical flasks containing varying amounts of pure cobalt nitrate solution and the volume adjusted to 20 ml with distilled water. The flasks were shaken for three hours at 30°C in the first set of experiment and 50°C in the second set of experiment, in an electric temperature controlled SICO shaker. The suspension were then centrifuged at 5000 rpm for 10 minutes and cobalt(II) was estimated in the supernatant liquid by a spectrophotometer at 530 nm. Amount of Cobalt(II) sorbed was determined as the difference between the amount of cobalt(II) added and that left after equilibrium.

The distribution coefficient values (Kd) were determined by using the formula

$$Kd = \frac{I - F}{F} \times \frac{\text{Total Volume of Solution (ml)}}{\text{Weight of the soil (gram)}} \quad ..(3)$$

where 'I' and 'F' are amount of cobalt(II) added and that present in the solution after equilibrium respectively.

II.3 RESULTS

The composition and physico-chemical properties of the two soils are presented in Table 2.1. The results for the effect of time on the sorption of Cobalt(II) on the two soils are presented in Tables 2.2 and 2.3 and plotted in Fig. 2.1.

The sorption isotherms of Cobalt(II) on the two soils are plotted in Fig. 2.2 and the results are given in Tables 2.4 - 2.7. The plots for Langmuir isotherms are presented in Fig. 2.3 and Fig. 2.4 and the values of Langmuir constants 'K' and 'b' are given in Table 2.12.

The thermodynamic equilibrium constant, Ko, is obtained from the plots of ln Cs/Ce versus Cs, for the two soils. The plots of ln Cs/Ce versus Cs are presented in Figs. 2.5 and 2.6 and their values are given in Tables 2.8 - 2.11. The enthalpy change was evaluated from the plot of lnKo versus 1/T and is presented in Fig. 2.7. The values of various thermodynamic parameters are summarized in Table 2.13.

TABLE 2.1

Composition and Physico-chemical properties of the two Indian Soils

Property	Bhopal	Tehri
% Sand	14.85	50.20
% Silt	49.15	30.80
% Clay	36.00	19.00
Texture	Silt Clay Loam	Loam
pH	8.50	6.30
Electrical Conductance S m^{-1}	4.32×10^{-4}	0.56×10^{-4}
% Organic matter	0.98268	1.1895
% Organic Carbon	0.57	0.6899
% $CaCO_3$	4.60	2.65
Cation Exchange Capacity [C mol P^+ Kg^{-1}]	23.80	5.80
Bulk Density gm/cm^3	1.38	1.56
Surface Area m^2 gm^{-1}	240.96	234.96
Porosity	0.43	0.38

TABLE 2.2

Effect of time on Bhopal Soil

Equilibrium time in minutes	Amount Added in µgm	Amount in µgm in total suspension	Amount (µgm) sorbed per gm soil x/m
5	5000	3595	1405
15	5000	3122	1878
30	5000	2666	2334
45	5000	1520	3480
60	5000	668	4332
90	5000	240	4760
120	5000	116	4884
180	5000	118	4882
240	5000	114	4886

TABLE 2.3

Effect of time on Tehri Soil

Equilibrium time in minutes	Amount Added in µgm	Amount in µgm in total suspension	Amount (µgm) sorbed per gm soil x/m
5	5000	3808	1192
15	5000	3496	1504
30	5000	2894	2106
45	5000	2148	2852
60	5000	1532	3468
90	5000	992	4008
120	5000	798	4202
180	5000	792	4208
240	5000	786	4214

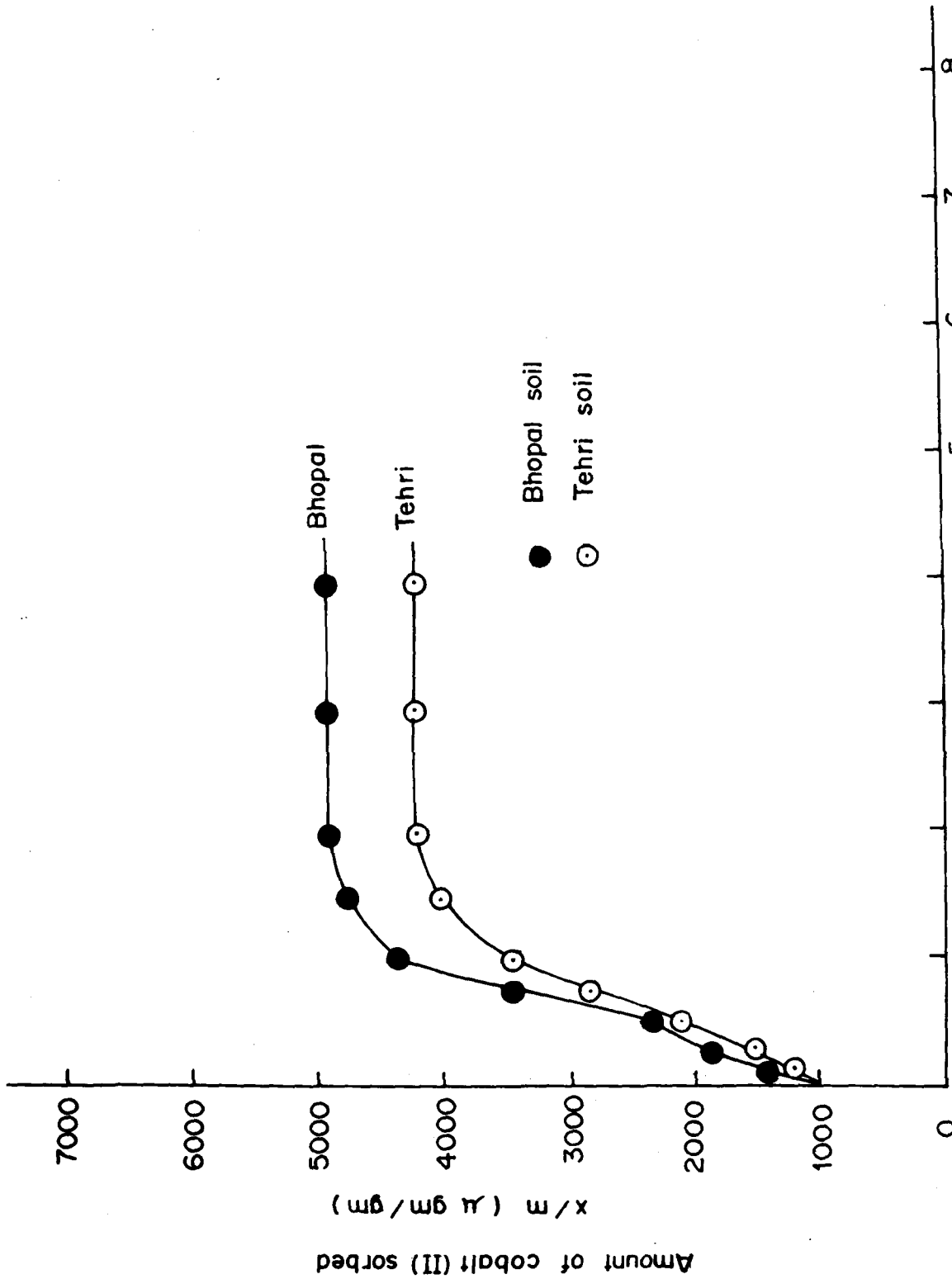

Fig. 2.1: Time dependence of sorption of cobalt (II) on Indian soils at 25°c.

TABLE 2.4

Sorption of Cobalt(II) on Tehri Soil at 30°C

Amount Added µgm/ml	Amount in equilibrium concentration Ce/20ml	Ce/ml	Amount sorbed per gram soil x/m	$\frac{Ce}{x/m}$	% Sorption	$Kd = \frac{I-F}{F} \times \frac{V}{W}$	Statistical Kd
100	0	0	100	0	100	-E-	
200	0	0	200	0	100	-E-	
400	12	0.6	388	1.546×10^{-3}	97.0	646.66	
600	24	1.2	576	2.083×10^{-3}	96.0	480.00	
800	48	2.4	752	3.191×10^{-3}	94.0	313.33	
1000	64	3.2	936	3.418×10^{-3}	93.60	292.50	119.604
1200	112	5.6	1088	5.147×10^{-3}	90.66	194.28	
1400	136	6.8	1264	5.379×10^{-3}	90.28	185.88	
1600	168	8.4	1432	5.865×10^{-3}	89.50	170.47	
1800	196	9.8	1604	6.109×10^{-3}	89.11	163.67	
2000	240	12.0	1760	6.818×10^{-3}	88.00	146.66	
2500	308	15.4	2192	7.025×10^{-3}	87.68	142.33	
3000	396	19.8	2604	7.603×10^{-3}	86.80	131.51	
3500	496	24.8	3004	8.255×10^{-3}	85.82	121.12	
4000	580	29.0	3420	8.479×10^{-3}	85.50	117.93	
4500	684	34.2	3816	8.962×10^{-3}	84.80	111.57	
5000	792	39.6	4208	9.410×10^{-3}	84.16	106.26	

TABLE 2.5

Sorption of cobalt(II) on Tehri Soil at 50°C

Amount Added µgm/ml	Amount in equilibrium concentration Ce/20ml	Ce/ml	Amount sorbed per gram soil x/m	$\frac{Ce}{x/m}$	% Sorption	$Kd = \frac{I-F}{F} \times \frac{V}{W}$	Statistical Kd
100	0	0	100	0	100	-E-	
200	0	0	200	0	100	-E-	
400	16	0.8	384	2.083×10^{-3}	96.00	480.0	
600	40	2.0	560	3.571×10^{-3}	93.33	280.0	106.374
800	92	4.6	708	6.497×10^{-3}	88.50	153.91	
1000	140	7.0	860	8.139×10^{-3}	86.00	122.85	
1200	176	8.8	1024	8.593×10^{-3}	85.33	116.36	
1400	208	10.4	1192	8.724×10^{-3}	85.14	114.61	
1600	244	12.2	1356	8.997×10^{-3}	84.75	111.14	
1800	276	13.8	1524	9.055×10^{-3}	84.66	110.43	
2000	312	15.6	1688	9.241×10^{-3}	84.40	108.20	
2500	392	19.6	2108	9.297×10^{-3}	84.32	107.55	
3000	476	23.8	2524	9.429×10^{-3}	84.13	106.05	
3500	556	27.8	2944	9.442×10^{-3}	84.11	105.89	
4000	636	31.8	3364	9.453×10^{-3}	84.10	105.78	
4500	716	35.8	3784	9.461×10^{-3}	84.08	105.69	
5000	810	40.5	4190	9.665×10^{-3}	84.00	103.45	

TABLE 2.6

Sorption of Cobalt(II) on Bhopal Soil at 30°C

Amount Added µgm/ml	Amount in equilibrium concentration Ce/20ml	Ce/ml	Amount sorbed per gram soil x/m	$\frac{Ce}{x/m}$	% Sorption	$Kd = \frac{I-F}{F} x \frac{V}{W}$	Statistical Kd
100	0	0	100	0	100.00	-E-	
200	0	0	200	0	100.00	-E-	
400	0	0	400	0	100.00	-E-	
600	0	0	600	0	100.00	-E-	
800	24	1.2	776	1.546×10^{-3}	97.00	646.66	
1000	40	2.0	960	2.083×10^{-3}	96.00	480.00	
1200	64	3.2	1136	2.816×10^{-3}	94.60	355.00	
1400	96	4.8	1304	3.680×10^{-3}	93.14	271.66	136.418
1600	138	6.9	1462	4.719×10^{-3}	91.37	211.88	
1800	168	8.4	1632	5.147×10^{-3}	90.66	194.28	
2000	200	10.0	1800	5.555×10^{-3}	90.00	180.00	
2500	260	13.0	2240	5.803×10^{-3}	89.60	172.30	
3000	330	16.5	2670	6.179×10^{-3}	89.00	161.81	
3500	430	21.5	3070	7.003×10^{-3}	87.71	142.79	
4000	514	25.7	3486	7.372×10^{-3}	87.15	135.64	
4500	618	30.9	3882	7.959×10^{-3}	86.26	125.63	
5000	726	36.3	4274	8.493×10^{-3}	85.48	117.74	

TABLE 2.7

Sorption of Cobalt(II) on Bhopal Soil at 50°C

Amount Added µgm/ml	Amount in equilibrium concentration Ce/20ml	Ce/ml	Amount sorbed per gram soil x/m	$\frac{Ce}{x/m}$	% Sorption	$Kd = \frac{I-F}{F} \times \frac{V}{W}$	Statistical Kd
100	0	0	100	0	100.00	-E-	
200	0	0	200	0	100.00	-E-	
400	8	0.4	392	1.020×10^{-3}	98.00	980.00	
600	28	1.4	572	2.447×10^{-3}	95.33	408.57	
800	56	2.8	744	3.763×10^{-3}	93.00	265.71	
1000	80	4.0	920	4.347×10^{-3}	92.00	230.00	
1200	128	6.4	1072	5.970×10^{-3}	89.33	167.50	
1400	160	8.0	1240	6.451×10^{-3}	88.57	155.00	115.176
1600	192	9.6	1408	6.818×10^{-3}	88.00	146.66	
1800	228	11.4	1572	7.251×10^{-3}	87.33	137.89	
2000	268	13.4	1732	7.736×10^{-3}	86.60	129.25	
2500	332	16.6	2168	7.656×10^{-3}	86.72	130.60	
3000	420	21.0	2580	8.139×10^{-3}	86.00	122.85	
3500	520	26.0	2980	8.724×10^{-3}	85.14	114.61	
4000	604	30.2	3396	8.892×10^{-3}	84.90	112.45	
4500	698	34.9	3802	9.179×10^{-3}	84.48	108.93	
5000	792	39.6	4208	9.410×10^{-3}	84.16	106.26	

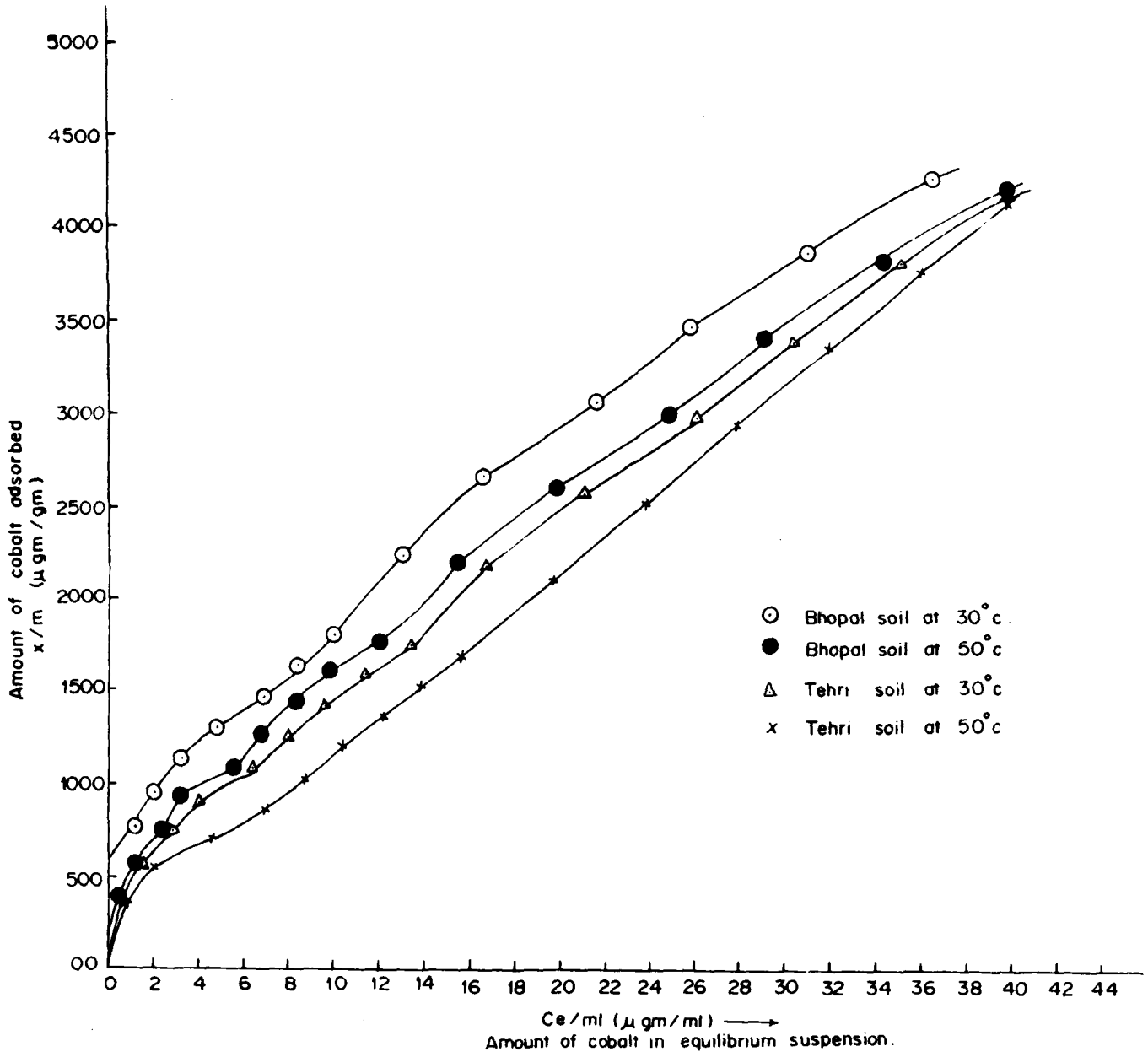

Fig. 2.2 : Sorption isotherms of cobalt(II) on two Indian soils at 30°c and 50°c

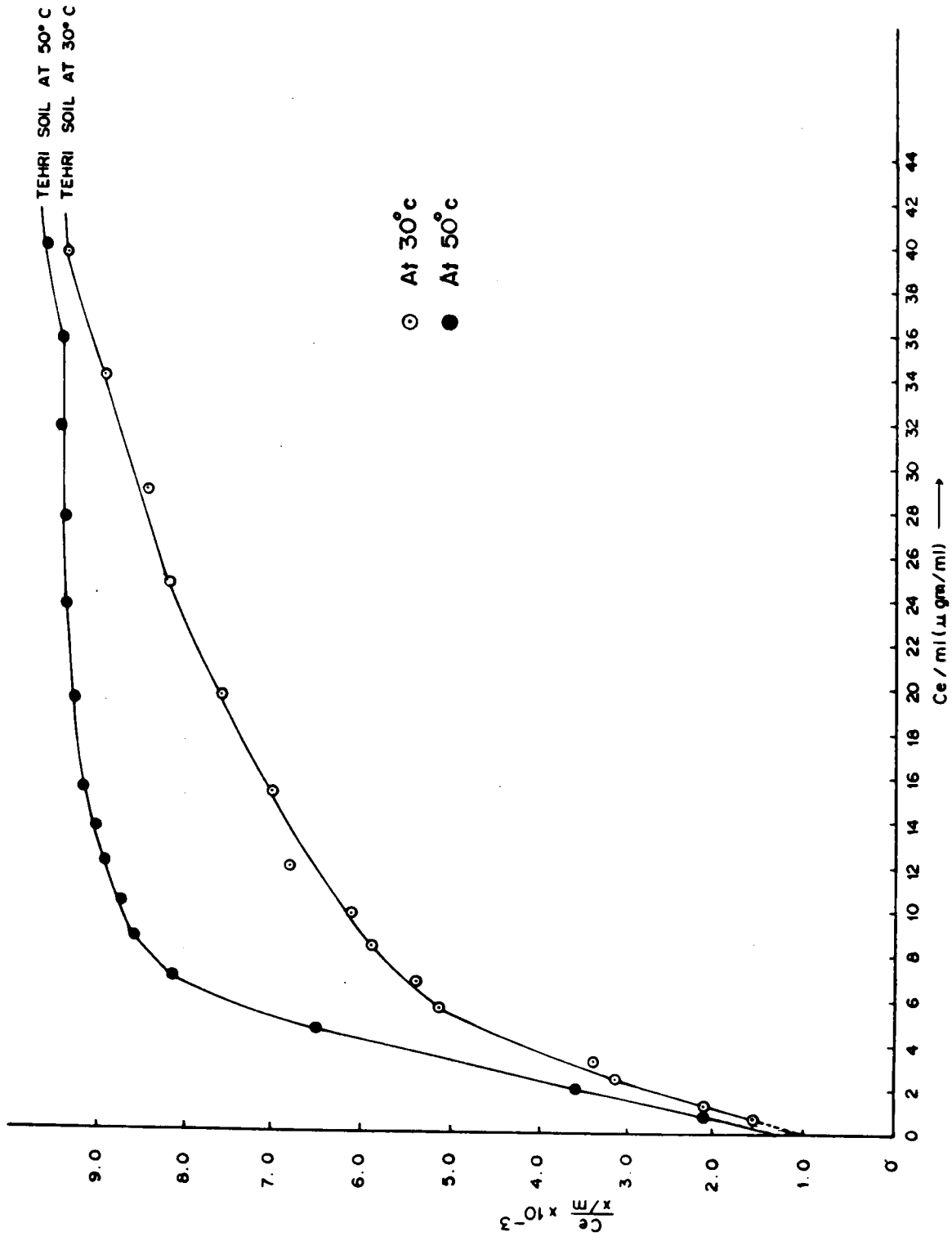

Fig.2.3: Test of langmuir isotherm for Cobalt (II) on Tehri soil at 30°C and 50°C.

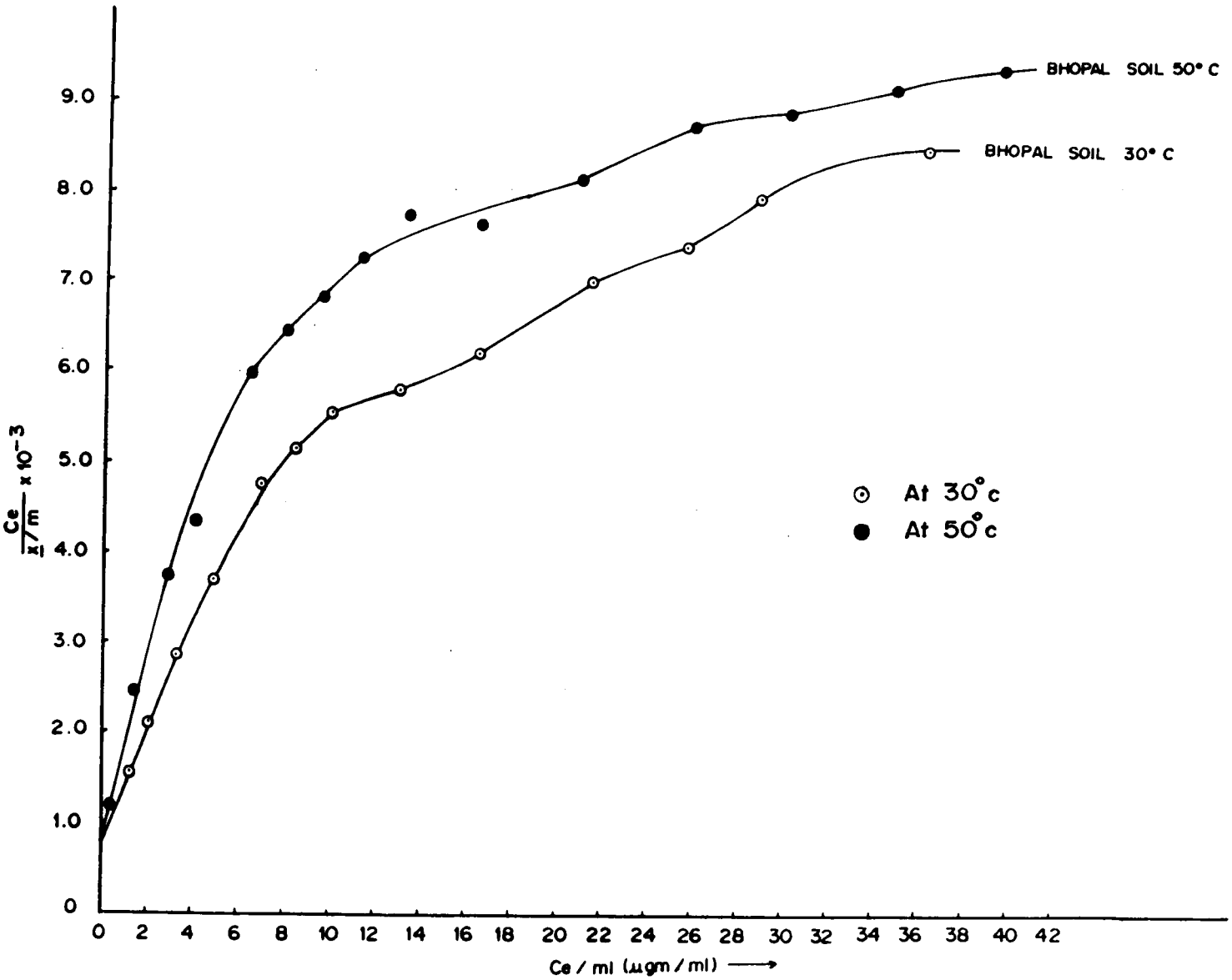

Fig.2.4 : Test of Langmuir isotherm for Cobalt (II) on Bhopal soil at 30°C and 50°C

TABLE 2.8

Values of Cs, ln $\frac{Cs}{Ce}$, for Tehri Soil at 30°C

Amount Added µgm/ml	Cs µgm gm^{-1}	Cs/Ce	ln $\frac{Cs}{Ce}$
100	51.2606	-E-	-E-
200	102.5213	-E-	-E-
400	198.8913	96475578	18.3848
600	295.2614	71610739	18.0867
800	385.4801	46745898	17.6602
1000	479.7998	43637794	17.5914
1200	557.7160	28985299	17.1822
1400	647.9347	27731609	17.1380
1600	734.0527	25433179	17.0515
1800	822.2210	24418288	17.0108
2000	902.1876	21881059	16.9011
2500	1123.6338	21235219	16.8711
3000	1334.8277	19620618	16.7921
3500	1539.8696	18071115	16.7098
4000	1753.1055	17593925	16.6831
4500	1956.1070	16646356	16.6277
5000	2157.0347	15853116	16.5788

TABLE 2.9

Values of Cs, ln $\frac{Cs}{Ce}$, for Tehri Soil at 50°C

Amount Added µgm/ml	Cs µgm gm^{-1}	Cs/Ce	ln $\frac{Cs}{Ce}$
100	51.2606	-E-	-E-
200	102.5213	-E-	-E-
400	196.8409	71610738	18.0867
600	287.0597	41772931	17.5477
800	362.9255	22962138	16.9493
1000	440.8417	18328939	16.7239
1200	524.9092	17360179	16.6696
1400	611.0271	17099359	16.6545
1600	695.0946	16581995	16.6238
1800	781.2125	16475659	16.6173
2000	865.2799	16143018	16.5970
2500	1080.5748	16045433	16.5900
3000	1293.8191	15821560	16.5800
3500	1509.1068	15798937	16.5750
4000	1724.4015	15782070	16.5740
4500	1939.6962	15768971	16.5730
5000	2147.8149	15434569	16.5500

TABLE 2.10

Values of Cs, ln $\frac{Cs}{Ce}$, for Bhopal Soil at 30°C

Amount Added µgm/ml	Cs µgm gm^{-1}	Cs/Ce	ln $\frac{Cs}{Ce}$
100	49.9842	-E-	-E-
200	99.9685	-E-	-E-
400	199.9370	-E-	-E-
600	299.9055	-E-	-E-
800	387.8778	94073293	18.3596
1000	479.8488	69827602	18.0615
1200	567.8211	51643330	17.7599
1400	651.7946	39520484	17.4923
1600	730.7698	30823658	17.2438
1800	815.7430	28263553	17.1571
2000	899.7165	26185351	17.0807
2500	1119.6473	25066318	17.0370
3000	1334.5796	23540366	16.9742
3500	1534.5052	20772204	16.8491
4000	1742.4459	19732353	16.7977
4500	1940.3781	18275976	16.7211
5000	2136.3173	17128204	16.6562

TABLE 2.11

Values of Cs, ln $\frac{Cs}{Ce}$, for Bhopal Soil at 50°C

Amount Added µgm/ml	Cs µgm gm^{-1}	Cs/Ce	ln $\frac{Cs}{Ce}$
100	49.9842	-E-	-E-
200	99.9685	-E-	-E-
400	195.9382	142564690	18.7753
600	285.9099	59436589	17.9004
800	371.8828	38654565	17.4701
1000	459.8551	33459060	17.3258
1200	535.8312	24366925	17.0087
1400	619.8047	22548496	16.9312
1600	703.7782	21336212	16.8759
1800	785.7524	20060122	16.8142
2000	865.7272	18803079	16.7495
2500	1083.6586	18999277	16.7599
3000	1289.5937	17872541	16.6988
3500	1489.5246	16673509	16.6290
4000	1697.4508	16358479	16.6103
4500	1900.3872	15847813	16.5785
5000	2103.3237	15458367	16.5536

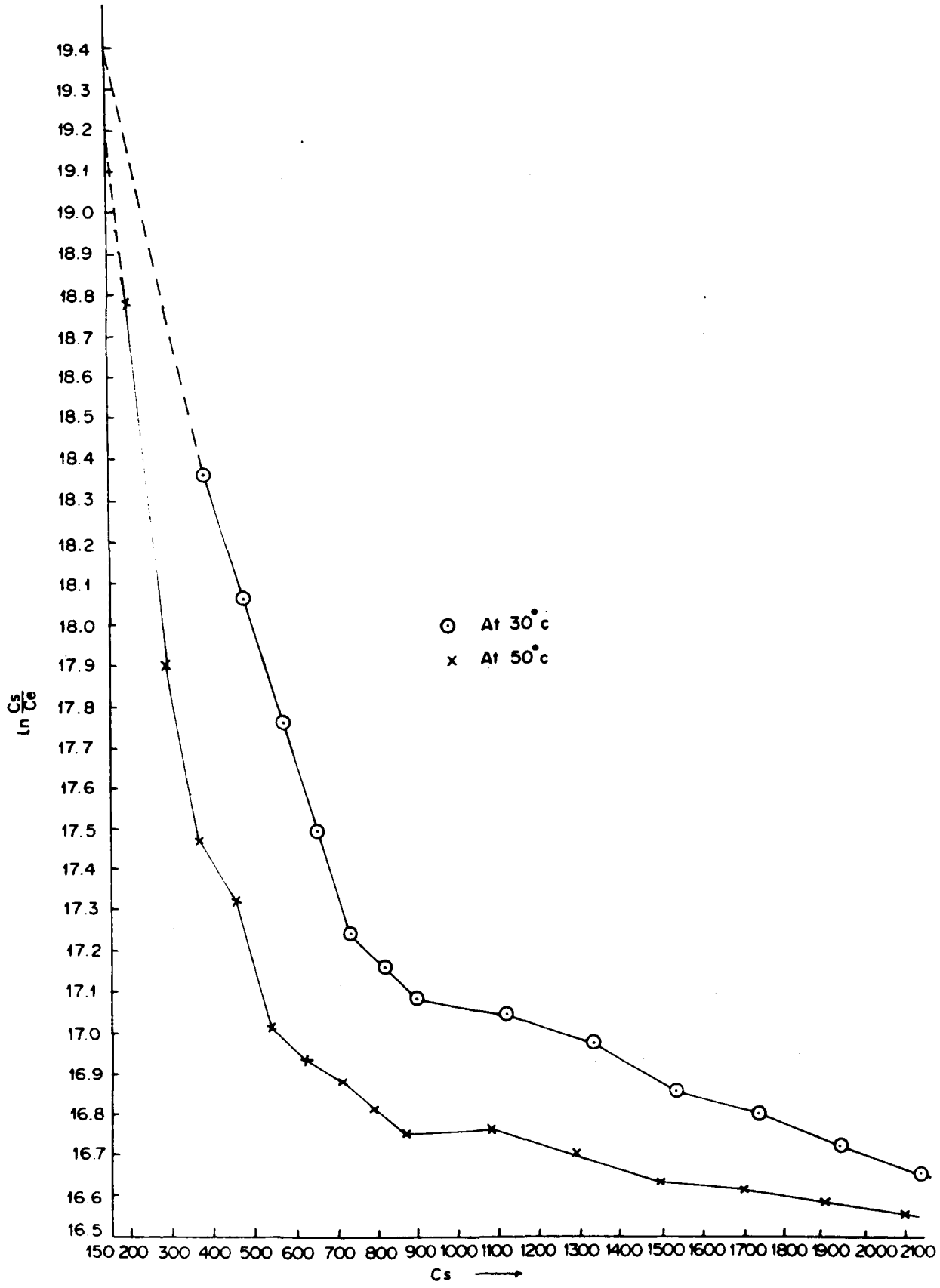

Fig. 2.5: Plots of $\ln \frac{Cs}{Ce}$ versus Cs for cobalt(II) on Bhopal soil

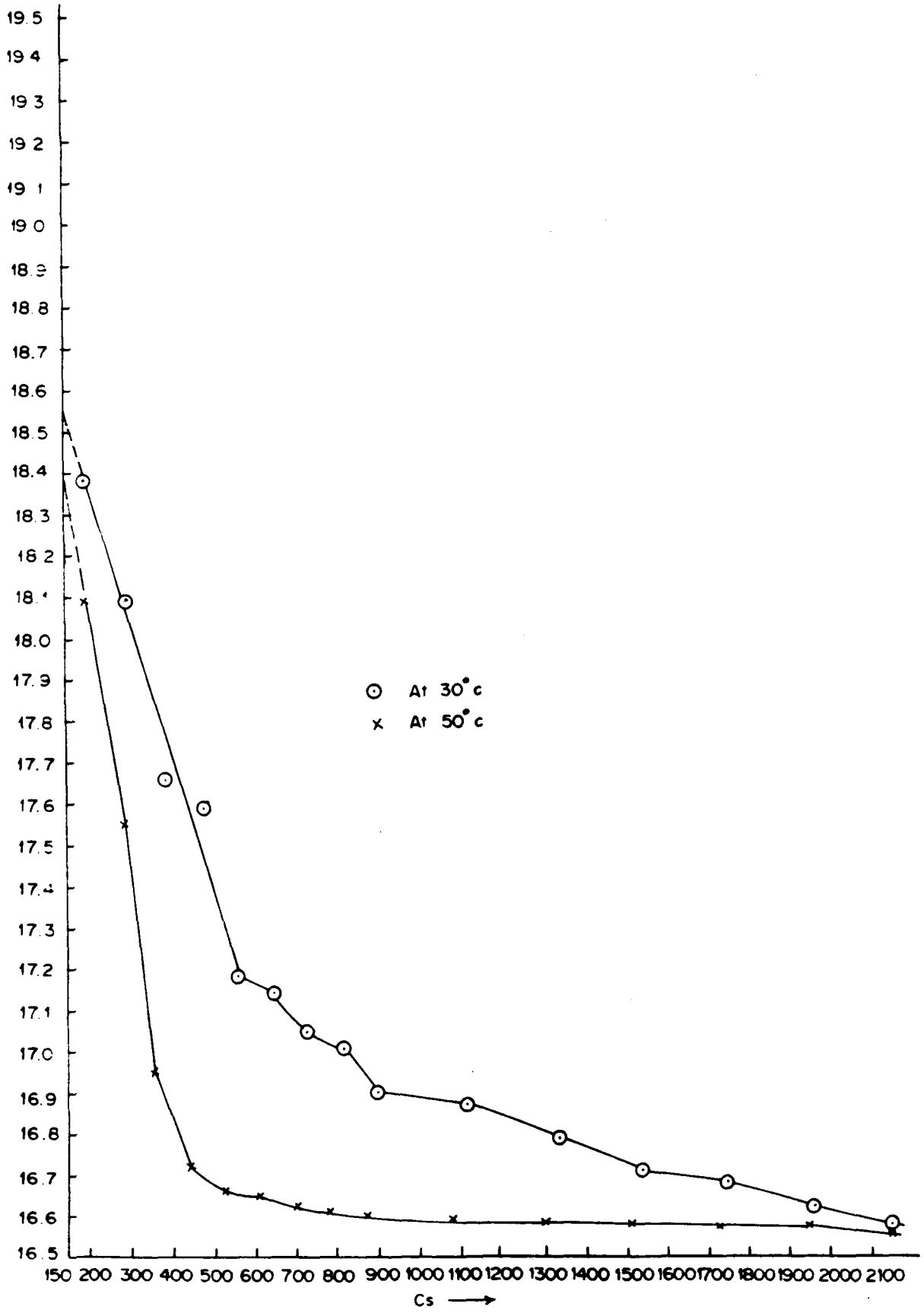

Fig.2.6 : Plots of $\ln \frac{Cs}{Ce}$ versus Cs for cobalt (II) on Tehri soil .

TABLE 2.12

Langmuir Constants, K and b at 30°C and 50°C

Soil Source	30°C K	30°C b	50°C K	50°C b
Bhopal	0.00133	1.53846×10^{3}	0.00176	1.14285×10^{3}
Tehri	0.000952	1.11111×10^{3}	0.00080	1.05263×10^{3}

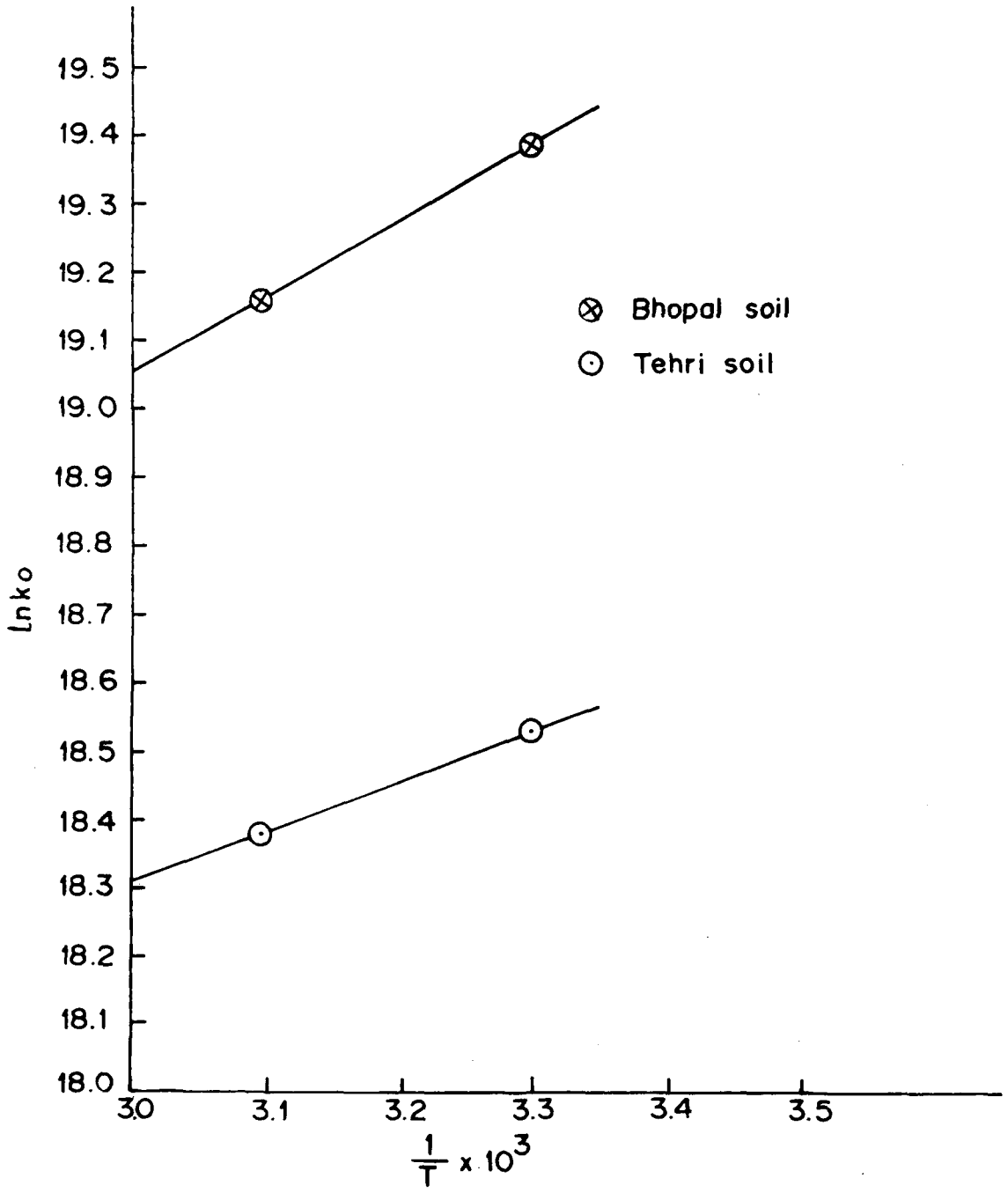

Fig. 2.7 : Determination of enthalpy of sorption of cobalt(II) on Indian soils .

TABLE 2.13

Various thermodynamic parameters for the sorption of Cobalt(II) on the soils

Thermodynamic Parameter	Bhopal Soil		Tehri Soil	
	30°C	50°C	30°C	50°C
Ko	2.6361×10^{8}	2.0945×10^{8}	1.1155×10^{8}	9.6013×10^{7}
$\Delta G°$ ($KJmol^{-1}$)	-48.8226	-51.4279	-46.6572	-49.3343
$\Delta H°$ ($KJmol^{-1}$)	-9.4971		-6.2325	
$\Delta S°$ ($KJK^{-1}mol^{-1}$)	0.1297	0.1297	0.1334	0.1334

II.4 DISCUSSION

The two soils under investigation were so chosen that they varied widely in their properties. It is evident from table 2.1 that the pH, electrical conductance and cation exchange capacity of Bhopal soil were higher than that of Tehri soil.

The results of the effect of equilibrium time on the sorption of cobalt(II) by both the soils are presented in Fig. 2.1 and values are given in tables 2.2 and 2.3. The sorption of cobalt(II) on both the soils increased with increase in time and became constant after 2 hours for both the soils. A time period of 3 hours was chosen for sorption studies of cobalt(II) on the two soils to ensure equilibrium.

Sorption of cobalt(II) was studied by batch process in the concentration range 0-5000 μg/ml at 30°C and 50°C respectively for both Bhopal and Tehri soils. Sorption isotherms were plotted between the amount of cobalt(II) sorbed per gram soil (μg/gm) and the amount of cobalt(II) in equilibrium suspension (μg/ml) and are shown in Fig. 2.2. It is clear from Fig. 2.2 that sorption of cobalt(II) was higher on Bhopal soil than Tehri soil. The higher sorption of

cobalt(II) on Bhopal soil is due to its higher cation exchange capacity, pH and greater percentage of clay, however there is not much difference between the percentage of organic matter in the two soils. The sorption of cobalt(II) decreases with the rise in temperature in both the soils, partly due to the weakening of attractive forces between cobalt(II) and soil and partly due to enhancement of thermal energies of the adsorbate; thus making the attractive force between cobalt(II) and soil weaker for the sorption of cobalt(II) at the binding sites.

From sorption data, the distribution coefficient values Kd, given in tables 2.4-2.7 were determined by using the formula

$$Kd = \frac{I-F}{F} \times \frac{V}{W} \qquad \ldots\ldots(3)$$

where 'I' and 'F' are amount of cobalt(II) added (μgm/ml) and that present in the solution after equilibrium respectively. 'V' is the total volume of the solution (in ml) and 'W' the weight of the soil (gms). The statistical average of all the Kd values was calculated by using the formula

$$Kd = \frac{\sum x/m \times Ce}{\sum (Ce)^2} \qquad \ldots\ldots(4)$$

where x/m is the amount of cobalt(II) sorbed per gram soil and Ce is the amount of cobalt(II) left in the solution after equilibrium. The values are given in tables 2.2-2.7. The higher statistical Kd values of Bhopal soil than Tehri soil as shown in tables 2.4-2.7 also confirms higher sorption of cobalt(II) on Bhopal soil at both the temperatures.

An examination of Fig. 2.2 reveals that the sorption isotherms at both the temperatures are of L class [14] for both the soils. These isotherms indicate that the molecules are adsorbed flat on the surface.

The sorption behaviour of cobalt(II) in both the soils was in close agreement with the linear form of the Langmuir equation [15]

$$\frac{Ce}{x/m} = \frac{1}{Kb} + \frac{Ce}{b} \qquad \ldots.(5)$$

where K and b are constants which represent the binding energy coefficient and sorption maxima respectively.

The Langmuir constants K and b were obtained from the intercept and slope of Langmuir isotherms shown in Figs. 2.3 and 2.4 and their values are given in table 2.12. The higher values of the Langmuir constants for Bhopal soil than for the Tehri soil at both the temperatures also confirm higher sorption of cobalt(II) in Bhopal soil. Similarly, higher values of the constants at 30°C also suggest higher sorption of cobalt(II) at lower temperature on both the soils. These results are in accordance with those of Veith and Sposito [16] who studied the use of Langmuir equation in the interpretation of adsorption phenomena. Although, sorption process is primarily one of cation exchange, the Langmuir equation has been frequently applied to the sorption of heavy metal cations from solution by the soils [17].

The thermodynamic equilibrium constant (Ko) for the sorption of cobalt(II) on the soils was calculated by the Biggar and Cheung [18] method as applied by Singh et al. [19]

$$K_o = \frac{C_s}{C_e} \times \frac{\nu_s}{\nu_e} \qquad \ldots.(6)$$

where Cs (μg/gm) is the amount of cobalt(II) adsorbed

per gram of the solvent in contact with the soil, Ce (μgm/ml) the concentration of cobalt in equilibrium suspension, γs the activity coefficient of the adsorbed solute and γe the activity coefficient of the solute in equilibrium suspension.

The value of Cs was calculated by using the equation proposed by Fu et al. [20]

$$Cs = \frac{(\rho/M)\ A}{\frac{S}{N\ .\ x/m}} \qquad ...(7)$$

where ρ is the density of the solvent (gm/ml), M the molecular weight of the solvent, A the cross-sectional area of the solvent molecule (cm^2 $molecule^{-1}$), N the Avogadro's number, S the surface area of the adsorbent (m^2/gm) and x/m the specific adsorption (mmol/gm).

The cross-sectional area of the solvent molecule was calculated by using the equation [21]

$$A = 1.091 \times 10^{-16} \left(\frac{10^{24} M}{N \rho}\right)^{2/3} \qquad ...(8)$$

The ratio of the activity coefficients was assumed to

be unity in the dilute range studied [22]. As the concentration of solute in the solution approached zero, the activity coefficient approached unity. Equation (6) may than be written as

$$\lim_{Cs \longrightarrow o} \frac{Cs}{Ce} = Ko \qquad ....(9)$$

The values of thermodynamic equilibrium constant (Ko) were obtained by plotting ln Cs/Ce versus Cs and extrapolating to zero Cs. The plots of ln Cs/Ce versus Cs are shown in Figs.2.5 and 2.6 and their values are given in tables 2.8-2.11.

The standard free energy changes (ΔG°) during the sorption were calculated from the relationship

$$\Delta G^\circ = -RT \ln Ko \qquad ....(10)$$

where R is the universal gas constant and T the absolute temperature.

The standard enthalpy change (ΔH°) was calculated from the integrated form of the Van't Hoff equation

$$\ln \left(\frac{K_{T_2}}{K_{T_1}}\right) = - \frac{\Delta H^\circ}{R} \left(1/T_2 - 1/T_1\right) \quad ...(11)$$

and the standard entropy changes (ΔS°) were calculated from ΔH° and ΔG° values, using the equation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad ...(12)$$

The values of the thermodynamic equilibrium constant Ko, standard free energy changes ΔG°, standard enthalpy changes ΔH°, and standard entropy changes ΔS° at 30°C and 50°C for the sorption of cobalt(II) on both the soils are summarised in table 2.13. These results show higher values of Ko at 30°C than at 50°C for both the soils indicating the higher preference of cobalt(II) for the soils at lower temperature. However these values were higher for Bhopal soil than Tehri soil, which again confirms that sorption of cobalt(II) was higher in Bhopal soil at both the temperatures. The results (table 2.13) show negative values of ΔG° for the sorption of cobalt(II) on the soils at both the temperatures. The enthalpy change (ΔH°) was also negative for both the

soils, which further indicates that a decrease in temperature favoured adosrption. The results of free energy changes (ΔG°) values show that the ion exchange/sorption phenomena was spontaneous in nature. More negative values of ΔH° for Bhopal soil confirms that cobalt(II) was more strongly bound to Bhopal soil as compared to Tehri soil. The results of entropy changes (ΔS°) in table 2.13 show a loss in entropy, more during the sorption of cobalt(II) on Bhopal soil; indicating a greater order produced during the sorption/ion exchange phenomena. The positive values of entropy change suggests stability of the complex.

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CHAPTER III

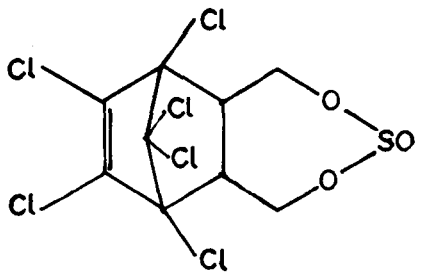
SORPTION OF PESTICIDE, ENDOSULPHAN ON TWO INDIAN SOILS - THE NATURAL ION EXCHANGERS

III.1 INTRODUCTION

Pesticides are indispensable in modern agriculture for increasing food production. However, their widespread use has led to a high content of pesticides in soils and water causing serious environmental pollution. Due to this reason environmental protection has become a major issue in agriculture during the last decade. Soils behave as natural ion exchangers. In the earlier studies sorption equilibria of Pb(II) on soils has been discussed [1]. The frequent detection of pesticides in surface and groundwater has greatly increased the experimental studies on pesticide adsorption by soils [2-4]. Adsorption is one of the most significant processes affecting bioactivity, mobility, persistence, toxicity and efficacy of pesticides in the soil environment [5,6]. Literature on this aspect has been reviewed by Bailey and White [7].

Endosulphan (hexachloro,hexahydro-6,9-methano 2,4,3-benzodioxathiepin-3-oxide) is a non-systemic most important contact and stomach insecticide because of its favourable toxicological action and low persistence in comparison to other chlorinated

pesticides. Its structure can be represented as :



Most of the data on pesticide adsorption by soils deal with aqueous solutions [8-15]. However, in some disposal operations, mixtures of chemical waste which are miscible in water reduce the adsorption. Recently, several workers [16-18], have focused on adsorption of certain pesticides from non-aqueous solvents and solvent mixtures, but information of this type of study is not available in literature on endosulphan adsorption by soil. This research created an adsorption system consisting of a liquid phase water with an organic solvent, soil and the test solute; endosulphan, to determine the influence of organic solvents methanol and acetone on endosulphan adsorption as measured by the batch equilibrium method and applicability of the co-solvent theory proposed by Rao et al. 1985 [19] was evaluated.

Methanol and acetone were used because they are completely miscible in water and are found in most waste streams from industrial wastes. Methanol is a proton donor while acetone is a proton acceptor [20]. These studies will provide information in assessing endosulphan movement in soil in the event of spill or discharge of organic wastes containing water soluble solvents.

III.2 EXPERIMENTAL

III.2.1 Collection of Soil Samples : The surface soil samples (0-30 cms) of silt clay loam and sandy loam soils were collected from Bhopal district of Madhya Pradesh and Mukteshwar district of Uttar Pradesh, India; respectively. The soils were dried, crushed and sieved and their physico-chemical properties were determined by the standard techniques as mentioned in experimental portion of chapter 2 of this thesis. The physico-chemical properties of the two soils are summarised in table 3.1.

III.2.2 Reagents : Endosulphan was obtained from Indo-Gulf fertilizers and chemicals corporation limited, Sultanpur (U.P.). All other chemicals and reagents used were of analytical reagent grade.

III.2.3 Apparatus : An electric temperature controlled SICO shaker was used for shaking; an Elico pH meter model Li-10 was used for pH measurements; Beckmann model L3-50 ultracentrifuge was used for centrifugation; a systronic conductivity meter dip type cell for electrical conductance measurements and Bausch and Lomb spectrophotometer model spectronic 20 for the determination of endosulphan.

III.2.4 Adsorption Studies : Stock solution of endosulphan of concentration 200 µgm/ml was prepared by dissolving requisite amount of endosulphan in methanol and acetone respectively.

Batch equilibrium adsorption isotherms were obtained in methanol-water and acetone-water systems. Four f_s values (0.25, 0.50, 0.75, 1.0) were utilised by taking eight concentrations of endosulphan (100, 200, 300, 400, 500, 600, 800 and 1000 µgm/ml) solutions in different flasks. The experiments were conducted in duplicate and each isotherm determination consists of sixteen flasks for each of eight endosulphan dose and one blank flask containing soil and no endosulphan. To these solutions 1 gm of each soil was added and suspensions were kept at 25°C in an incubator for 24 hours with shaking periods of three hours. There was no measurable increase in endosulphan adsorption beyond 12 hours in both cosolvents. The suspension were then centrifuged at 10,000 rpm for 10 minutes using Beckmann model L3-50 ultracentrifuge and in the supernatant endosulphan was estimated spectrophotometrically [22] to calculate the amount of endosulphan adsorbed.

III.3 RESULTS

The mechanical composition and the physico-chemical properties of the two soils are presented in table 3.1. The adsorption data are summarised in tables 3.2-3.17 and the adsorption isotherms are shown in Figs. 3.1 and 3.2.

The adsorption process was in agreement with the Freundlich isotherms shown in Figs. 3.3-3.6 for both the methanol-water system and acetone-water system. The values of Freundlich constants (K and 1/n) and Partition Coefficient (statistical Kd) are given in table 3.18 for both the systems. Selected properties of the acetone-water mixture and methanol-water mixture are presented in table 3.19.

The adsorption isotherm data K_m, K_{moc}, $LogK_{moc}$ used to evaluate the cosolvent theory, are presented in table 3.20.

Table 3.1

Composition and Physico-chemical properties of the soils

Properties	Sandy loam soil (Mukteshwar)	Silt clay loam soil (Bhopal)
% Sand	59.12	14.85
% Silt	34.80	49.15
% Clay	6.0	36.0
Texture	Sandy loam	Silt clay loam
pH	6.0	8.5
Electrical conductance ($S\ m^{-1}$)	2.833×10^{-4}	4.32×10^{-4}
% Organic matter	4.06002	0.98268
% Organic carbon	2.355	0.57
Cation Exchange Capacity [C mol $P^{+}\ Kg^{-1}$]	17.0	23.80
Bulk Density (gm/cm^3)	1.18	1.38
% $CaCO_3$	4.75	4.60
Surface Area (m^2/gm)	58.979	240.96
Porosity	0.33	0.43

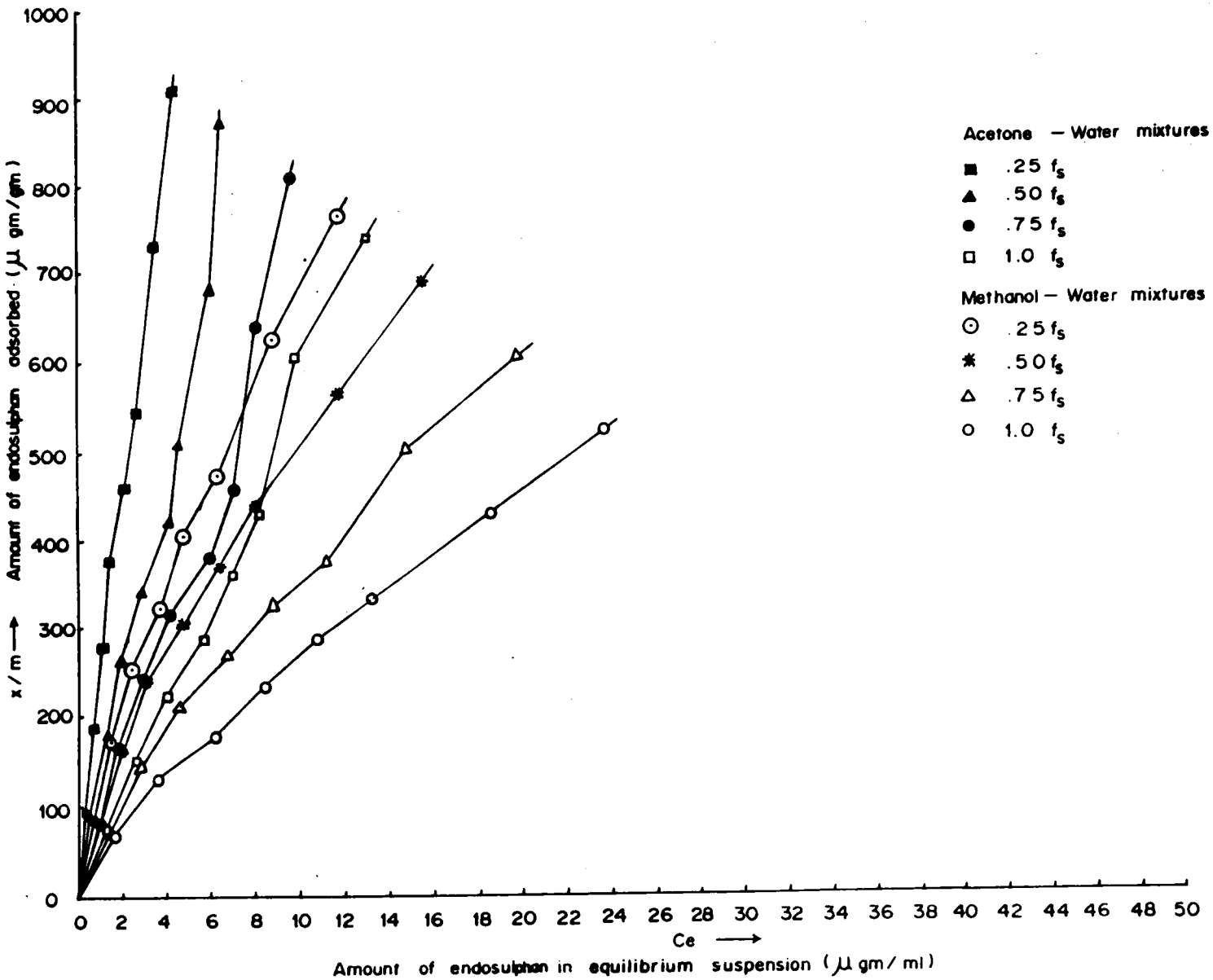


Fig. 3.1 : Adsorption isotherms of endosulphan on sandy loam soil at different f_s of cosolvents.

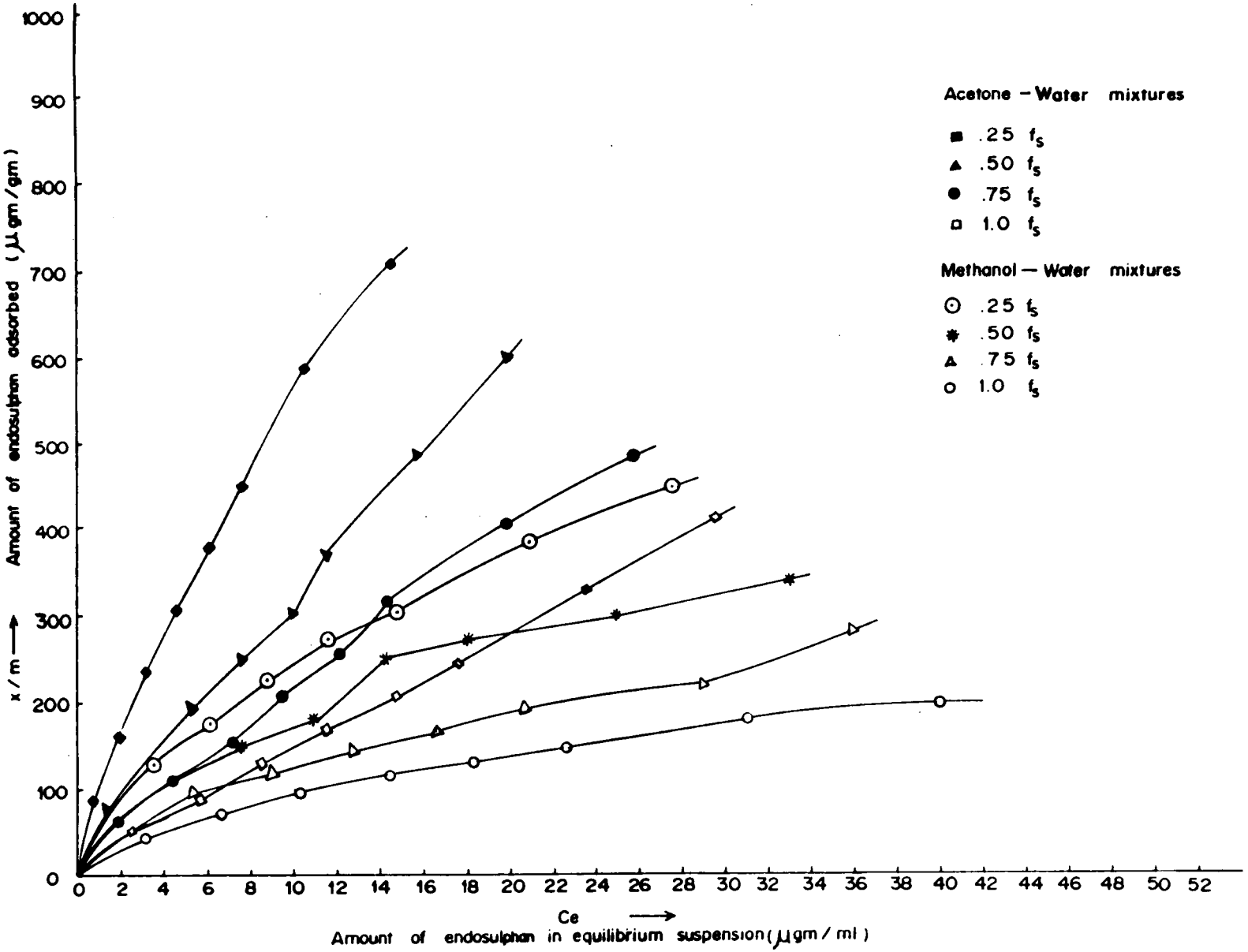


Fig. 3.2: Adsorption isotherms of endosulphan on silt clay loam soil at different f_s of cosolvents.

Table 3.2

Adsorption of Endosulphan on Mukteshwar Soil at 0.25 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \times \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	6	94	0.3	-0.5228	1.9731	313.333	
200	14	186	0.7	-0.1549	2.2695	265.714	
300	24	276	1.2	0.0792	2.4409	230.000	
400	28	372	1.4	0.1461	2.5705	265.714	209.55
500	42	458	2.1	0.3222	2.6602	218.095	
600	54	546	2.7	0.4313	2.7370	202.222	
800	70	730	3.5	0.5440	2.8633	208.571	
1000	90	910	4.5	0.6532	2.9590	202.222	

Table 3.3

Adsorption of Endosulphan on Mukteshwar Soil at 0.50 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \times \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	10	90	0.5	-0.3010	1.9542	180.000	
200	26	174	1.3	0.1139	2.2405	133.846	
300	40	260	2.0	0.3010	2.4149	130.000	
400	58	342	2.9	0.4623	2.5340	117.931	119.235
500	82	418	4.1	0.6127	2.6211	101.951	
600	92	508	4.6	0.6627	2.7058	110.434	
800	120	680	6.0	0.7781	2.8325	113.333	
1000	130	870	6.5	0.8129	2.9395	133.846	

Table 3.4

Adsorption of Endosulphan on Mukteshwar Soil at 0.75 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F}.\frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	20	80	1.0	0.0000	1.9030	80.000	
200	36	164	1.8	0.2552	2.2148	91.111	
300	60	240	3.0	0.4771	2.3802	80.000	
400	84	316	4.2	0.6232	2.4996	75.238	75.906
500	120	380	6.0	0.7781	2.5797	63.333	
600	142	458	7.1	0.8512	2.6608	64.507	
800	162	638	8.1	0.9084	2.8048	78.765	
1000	192	808	9.6	0.9822	2.9074	84.166	

Table 3.5

Adsorption of Endosulphan on Mukteshwar Soil at 1.0 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	24	76	1.2	0.0792	1.8808	63.333	
200	50	150	2.5	0.3979	2.1760	60.000	
300	78	222	3.9	0.5910	2.3463	56.923	
400	114	286	5.7	0.7558	2.4563	50.175	56.327
500	140	360	7.0	0.8450	2.5563	51.428	
600	164	436	8.2	0.9138	2.6394	53.170	
800	196	604	9.8	0.9912	2.7810	61.632	
1000	260	740	13.0	1.1139	2.8692	56.923	

Table 3.6

Adsorption of Endosulphan on Mukteshwar Soil at 0.25 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-f}{F}.\frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	12	88	0.6	-0.2218	1.9444	146.666	
200	32	168	1.6	0.2041	2.2253	105.000	
300	48	252	2.4	0.3802	2.4014	105.000	
400	76	324	3.8	0.5797	2.5105	85.263	71.550
500	96	404	4.8	0.6812	2.6063	84.166	
600	128	472	6.4	0.8061	2.6739	73.750	
800	176	624	8.8	0.9441	2.7951	70.909	
1000	234	766	11.7	1.0681	2.8842	65.407	

Table 3.7

Adsorption of Endosulphan on Mukteshwar Soil at 0.50 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F}.\frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	16	84	0.8	-0.0969	1.9242	105.000	
200	40	160	2.0	0.3010	2.2041	80.000	
300	60	240	3.0	0.4771	2.3802	80.000	
400	96	304	4.8	0.6812	2.4828	63.333	49.150
500	130	370	6.5	0.8129	2.5682	56.923	
600	162	438	8.1	0.9084	2.6414	54.074	
800	236	564	11.8	1.0710	2.7512	47.796	
1000	312	688	15.6	1.1931	2.8375	44.102	

Table 3.8

Adsorption of Endosulphan on Mukteshwar Soil at 0.75 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F}.\frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	24	76	1.2	0.0792	1.8805	63.333	
200	56	144	2.8	0.4471	2.1583	51.428	
300	92	208	4.6	0.6627	2.3180	45.217	
400	136	264	6.8	0.8325	2.4216	38.823	33.377
500	176	324	8.8	0.9444	2.5105	36.818	
600	224	376	11.2	1.0492	2.5751	33.571	
800	296	504	14.8	1.1702	2.7024	34.054	
1000	396	604	19.8	1.2966	2.7810	30.505	

Table 3.9

Adsorption of Endosulphan on Mukteshwar Soil at 1.0 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F}.\frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	32	68	1.6	0.2041	1.8325	42.500	
200	72	128	3.6	0.5563	2.1072	35.555	
300	124	176	6.2	0.7923	2.2455	28.387	
400	168	232	8.4	0.9242	2.3654	27.619	23.839
500	216	284	10.8	1.0334	2.4533	26.296	
600	260	340	13.0	1.1139	2.5314	26.153	
800	372	428	18.6	1.2695	2.6314	23.010	
1000	476	524	23.8	1.3765	2.7193	22.016	

Table 3.10

Adsorption of Endosulphan on Bhopal Soil at 0.25 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	16	84	0.8	-0.0969	1.9242	105.000	
200	40	160	2.0	0.3010	2.2041	80.000	
300	64	236	3.2	0.5051	2.3729	73.750	
400	94	306	4.7	0.6720	2.4857	65.106	54.772
500	122	378	6.1	0.7853	2.5774	61.967	
600	152	448	7.6	0.8808	2.6512	58.947	
800	210	590	10.5	1.0211	2.7708	56.190	
1000	290	710	14.5	1.1613	2.8512	48.965	

Table 3.11

Adsorption of Endosulphan on Bhopal Soil at 0.50 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	28	72	1.4	0.1461	1.8573	51.428	
200	64	136	3.2	0.5051	2.1335	42.500	
300	106	194	5.3	0.7242	2.2878	36.603	
400	152	248	7.6	0.8808	2.3944	32.631	31.078
500	200	300	10.0	1.0000	2.4771	30.000	
600	230	370	11.5	1.0606	2.5682	32.173	
800	316	484	15.8	1.1986	2.6848	30.632	
1000	398	602	19.9	1.2988	2.7795	30.251	

Table 3.12

Adsorption of Endosulphan on Bhopal Soil at 0.75 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	40	60	2.0	0.3010	1.7781	30.000	
200	88	112	4.4	0.6434	2.0492	25.454	
300	144	156	7.2	0.8573	2.1931	21.666	
400	190	210	9.5	0.9777	2.3222	22.105	20.208
500	244	256	12.2	1.0863	2.4082	20.983	
600	286	314	14.3	1.1553	2.4969	21.958	
800	398	402	19.9	1.2988	2.6042	20.201	
1000	514	486	25.7	1.4099	2.6866	18.910	

Table 3.13

Adsorption of Endosulphan on Bhopal Soil at 1.0 f_s in acetone-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	46	54	2.3	0.3617	1.7323	23.478	
200	108	92	5.4	0.7323	1.9638	17.037	
300	170	130	8.5	0.9293	2.1139	15.294	
400	230	170	11.5	1.0606	2.2304	14.782	14.142
500	296	204	14.8	1.1702	2.3096	13.783	
600	350	250	17.5	1.2430	2.3979	14.286	
800	470	330	23.5	1.3710	2.5185	14.042	
1000	590	410	29.5	1.4698	2.6127	13.898	

Table 3.14

Adsorption of Endosulphan on Bhopal Soil at 0.25 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F}.\frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	28	72	1.4	0.1461	1.8573	51.428	
200	70	130	3.5	0.5440	2.1139	37.142	
300	124	176	6.2	0.7923	2.2455	28.387	
400	176	224	8.8	0.9444	2.3502	25.454	18.869
500	232	268	11.6	1.0644	2.4281	23.103	
600	294	306	14.7	1.1673	2.4857	20.816	
800	418	382	20.9	1.3201	2.5820	18.277	
1000	550	450	27.5	1.4393	2.6532	16.363	

Table 3.15

Adsorption of Endosulphan on Bhopal Soil at 0.50 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m \cdot Ce}{\sum (Ce)^2}$
100	36	64	1.8	0.2552	1.8062	35.555	
200	90	110	4.5	0.6532	2.0413	24.444	
300	152	148	7.6	0.8808	2.1702	19.473	
400	220	180	11.0	1.0413	2.2552	16.363	12.285
500	286	224	14.3	1.1553	2.3304	15.664	
600	362	238	18.1	1.2576	2.3765	13.149	
800	500	300	25.0	1.3979	2.4770	12.000	
1000	660	340	33.0	1.5185	2.5314	10.303	

Table 3.16

Adsorption of Endosulphan on Bhopal Soil at 0.75 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	50	50	2.5	0.3979	1.6989	20.000	
200	108	92	5.4	0.7324	1.9638	17.037	
300	180	120	9.0	0.9524	2.0792	13.333	
400	254	146	12.7	1.1038	2.1640	11.496	8.616
500	300	170	16.5	1.2174	2.2300	10.303	
600	408	192	20.7	1.3096	2.2833	9.411	
800	580	220	29.0	1.4623	2.3424	7.586	
1000	720	280	36.0	1.5563	2.4471	7.770	

Table 3.17

Adsorption of Endosulphan on Bhopal Soil at 1.0 f_s in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	56	44	2.8	0.4471	1.6434	15.714	
200	132	68	6.6	0.8195	1.8325	10.303	
300	204	96	10.2	1.0086	1.9822	9.411	
400	288	112	14.4	1.1583	2.0492	7.770	5.979
500	366	134	18.3	1.2624	2.1271	7.322	
600	452	148	22.6	1.3541	2.1702	6.548	
800	620	180	31.0	1.4913	2.2552	5.806	
1000	800	200	40.0	1.6020	2.3010	5.000	

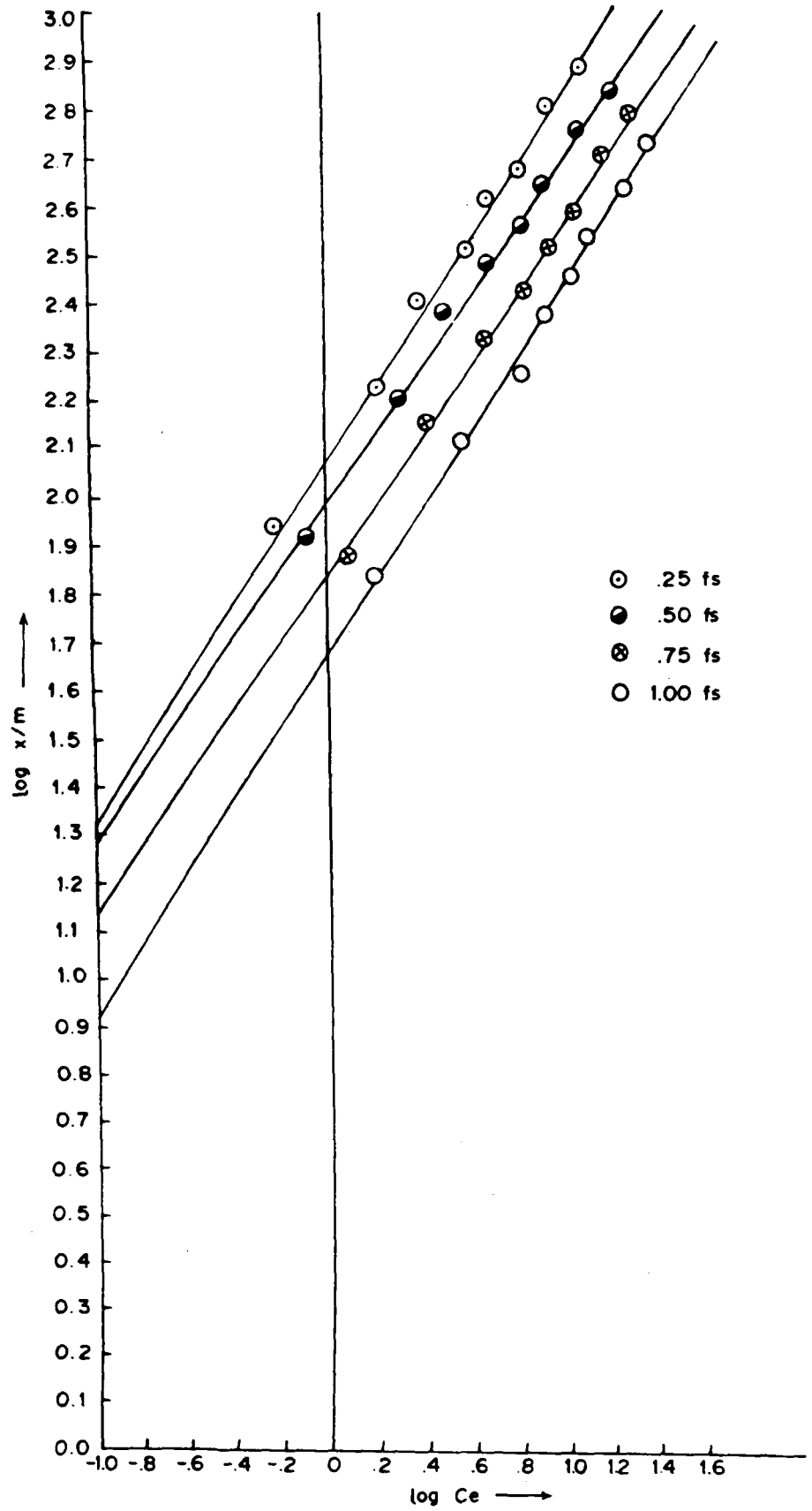


Fig.3.3 : Freundlich adsorption isotherms for sandy loam soil in methanol-water mixture.

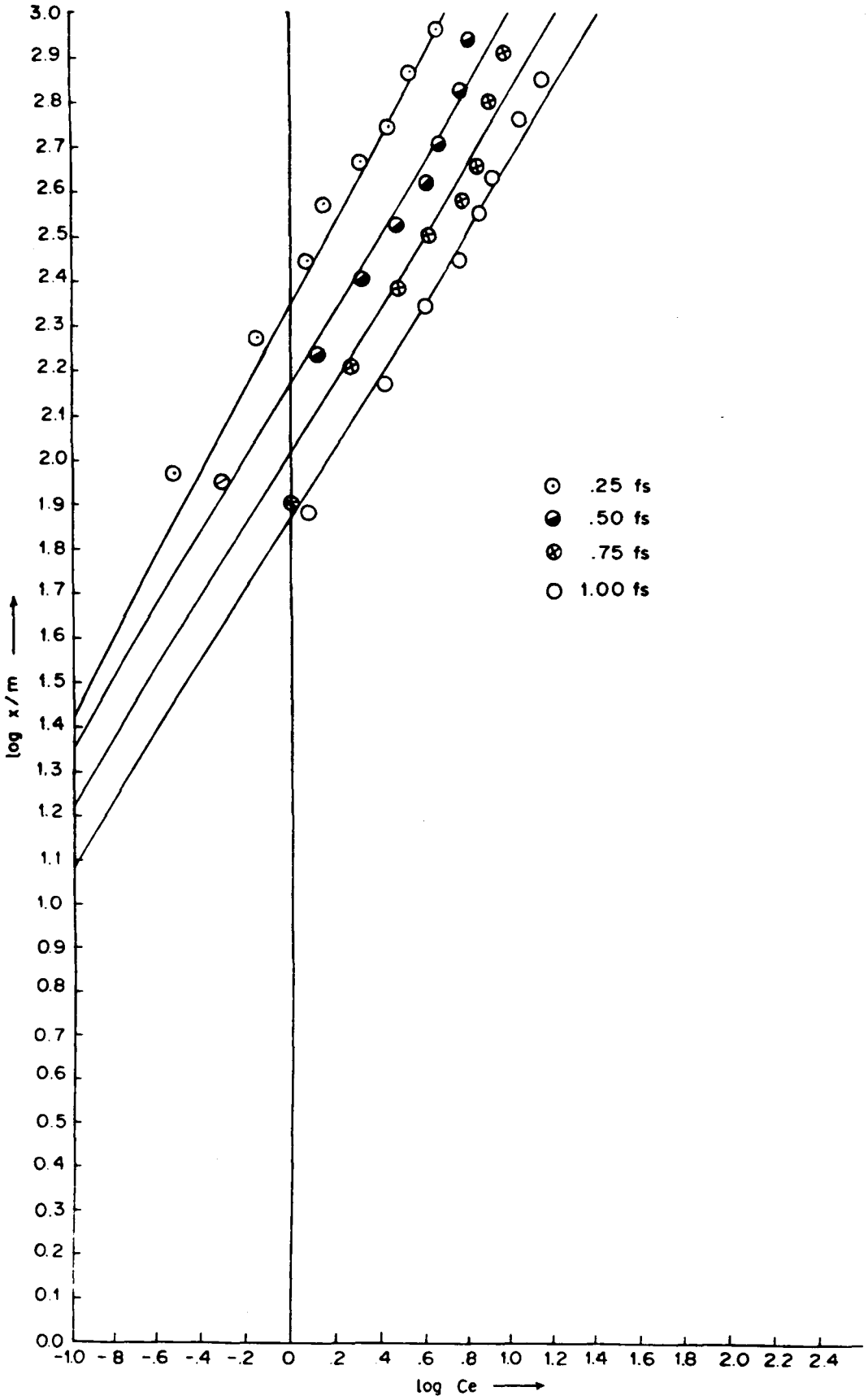


Fig. 3.4 : Freundlich adsorption isotherms for sandy loam soil in acetone-water mixture .

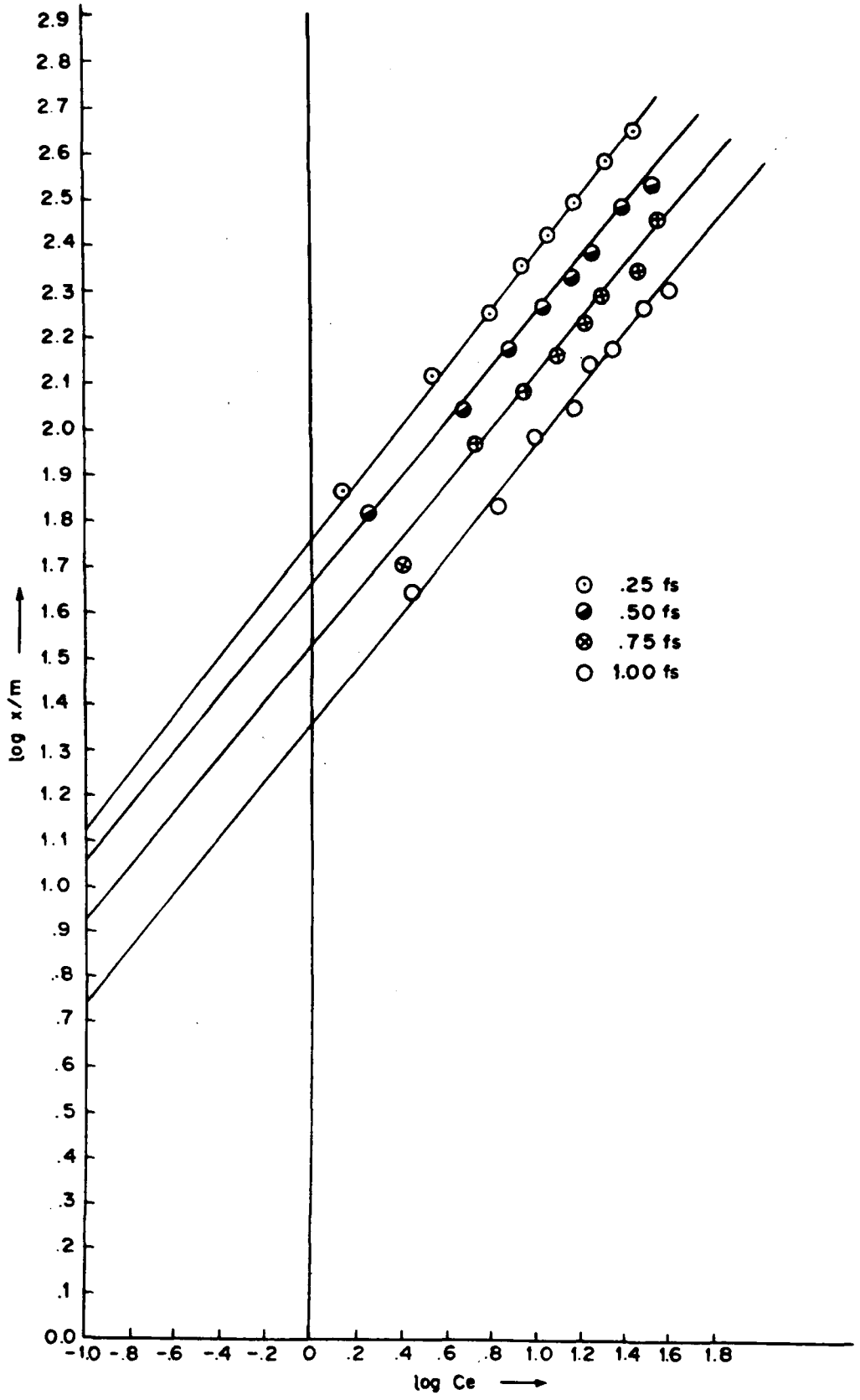


Fig. 3.5 : Freundlich adsorption isotherms for silt clay loam soil in methnol-water mixture.

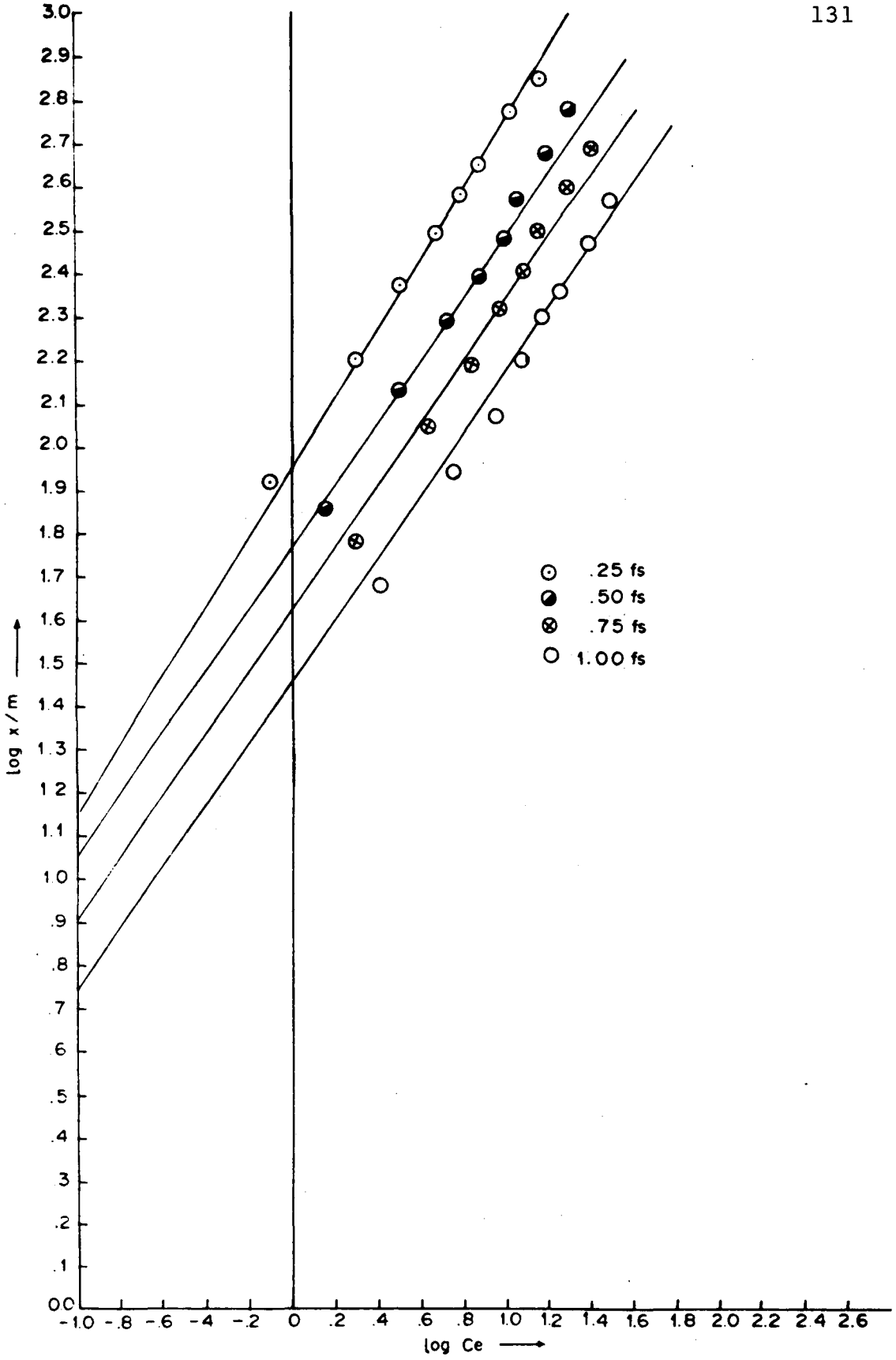


Fig. 3.6 : Freundlich adsorption isotherms on silt clay loam soil in acetone-water mixture .

Table 3.18

Freundlich Constants, Partition Coefficients data of Endosulphan Adsorption on Different Volume Fraction of Cosolvents

f_s	Statistical K_D	K	1/n	r^2	K_C	K_{om}
			Acetone-water mixture			
			Sandy loam (Mukteshwar) soil			
0.25	209.550	218.776	0.90	0.9947	3492.50	5161.304
0.50	119.235	147.910	0.85	0.9900	1987.25	2936.808
0.75	75.906	104.712	0.83	0.9875	1265.10	1869.596
1.00	56.327	74.131	0.83	0.9956	938.78	1387.357
			Silt Clay Loam (Bhopal) soil			
0.25	54.772	89.125	0.78	0.9851	152.14	5573.737
0.50	31.078	58.884	0.73	0.9960	86.32	3162.575
0.75	20.208	42.657	0.73	0.9950	56.13	2056.417
1.00	14.142	28.840	0.73	0.9978	39.28	1439.125
			Methanol-water mixture			
			Sandy Loam (Mukteshwar) soil			
0.25	71.550	117.489	0.73	0.9852	1192.50	1762.306
0.50	49.150	93.320	0.73	0.9773	819.16	1210.585
0.75	33.380	69.180	0.73	0.9876	556.33	822.163
1.00	23.839	46.770	0.73	0.9891	397.31	587.164
			Silt Clay Loam (Bhopal) soil			
0.25	18.869	56.234	0.62	0.9656	52.41	1920.157
0.50	12.285	44.668	0.60	0.9579	34.12	1250.152
0.75	8.616	33.113	0.60	0.9629	23.93	876.785
1.00	5.979	22.387	0.60	0.9586	16.61	608.438

Table 3.19

Selected properties of methanol-water mixture

Volume fraction of Cosolvent f_s	Mass fraction f_m	Mole fraction f_{mol}	Liquid density (gm/ml) P_{mix}	Molar volume (ml/mol) V
0.00	0.0000	0.0000	0.9998	18.00
0.25	0.2090	0.1300	0.9482	20.50
0.50	0.4422	0.3083	0.8965	24.10
0.75	0.7040	0.5722	0.8447	29.80
1.00	1.0000	1.0000	0.7913	40.40

Selected properties of acetone-water mixture

0.00	0.0000	0.0000	0.9998	18.00
0.25	0.2091	0.0757	0.9465	22.20
0.50	0.4424	0.1974	0.8950	28.95
0.75	0.7040	0.4245	0.8435	41.51
1.00	1.0000	1.0000	0.7920	73.33

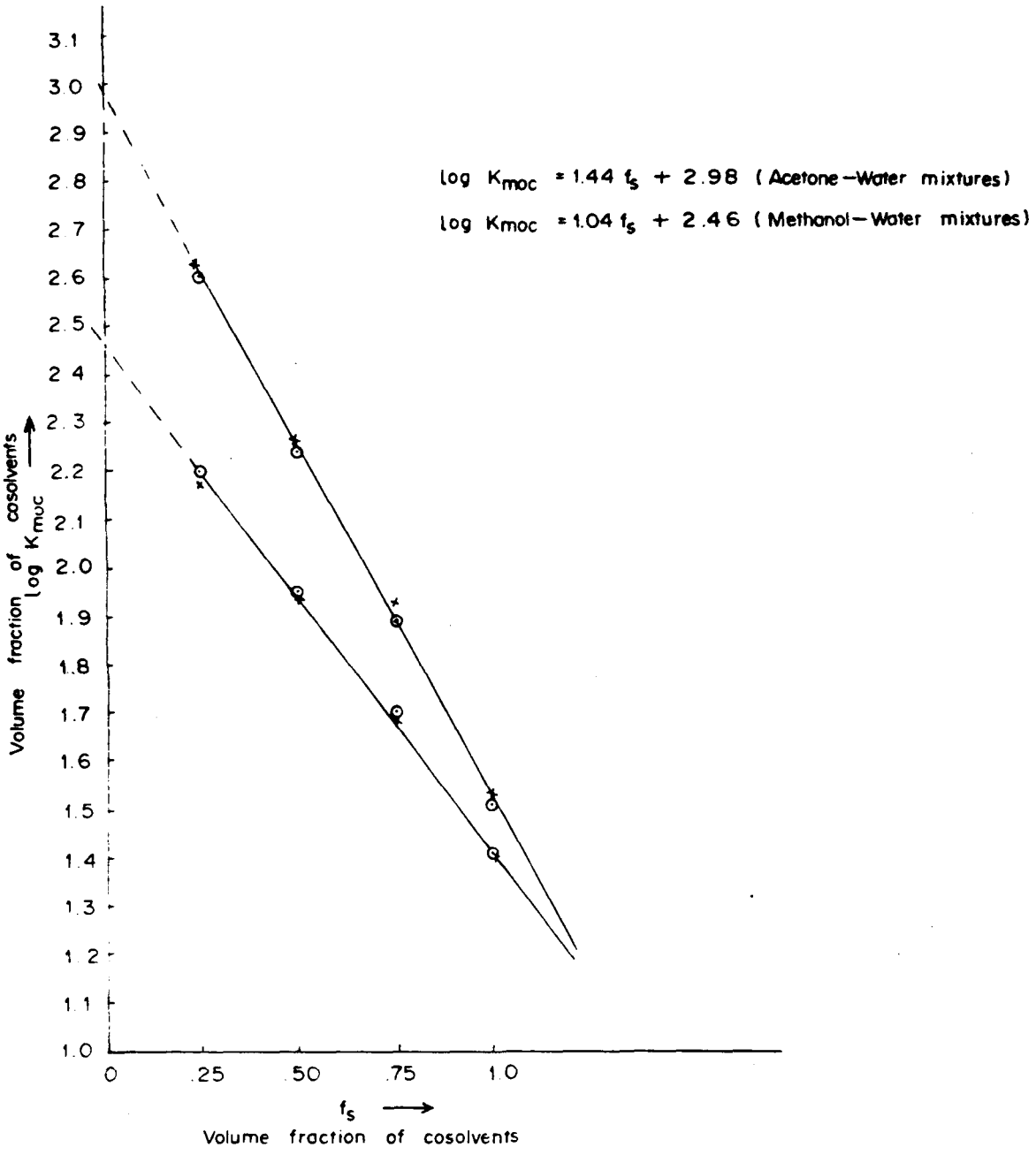


Fig. 3.7: Log linear plot of adsorption partition coefficients log K_{moc} Vs f_s

Table 3.20

Summary of the adsorption isotherm data used to evaluate the Cosolvent theory

f_s	Statistical K_D	n	K_m	K_{moc}	Log K_{moc}
			Acetone-water mixture		
			Sandy Loam (Mukteshwar) soil		
0.25	209.550	8	9.4391	400.814	2.60
0.50	119.235	8	4.1186	174.889	2.24
0.75	75.906	8	1.8286	77.648	1.89
1.00	56.327	8	0.7681	32.671	1.51
			Silt Clay Loam (Bhopal) soil		
0.25	54.772	8	2.4672	432.843	2.63
0.50	31.078	8	1.0735	188.334	2.27
0.75	20.208	8	0.4868	85.407	1.93
1.00	14.142	8	0.1928	33.834	1.53
			Methanol-water mixture		
			Sandy Loam (Mukteshwar) soil		
0.25	71.550	8	3.4900	148.195	2.17
0.50	49.150	8	2.0390	86.581	1.94
0.75	33.380	8	1.1203	47.559	1.68
1.00	23.839	8	0.5901	25.053	1.40
			Silt Clay Loam (Bhopal) soil		
0.25	18.869	8	0.9204	161.480	2.20
0.50	12.285	8	0.5097	89.430	1.95
0.75	8.616	8	0.2891	50.724	1.70
1.00	5.979	8	0.1479	25.964	1.41

III.4 DISCUSSION

The cosolvent theory was proposed by Rao et al. 1985 [19], to describe the adsorption of hydrophobic organic compounds to soils. The theory has been applied to the adsorption of several organic compounds having moderate and intermediate hydrophobicity by NKedi-Kizza et al. 1985 [21], Walters and Gulseppl-elle 1988 [16] and Fu and Luthy 1986 [23]. This theory is expressed by the equation

$$\text{Log} \left[K_{mi} / K_{wi} \right] = -\alpha \sigma_s \qquad \ldots.(1)$$

where K_{mi} and K_{wi} are the mole-based partition coefficients (mol/gm) for water-cosolvents (methanol and acetone) mixtures and cosolvents free water, respectively. The term σ_s reflects the solute-liquid interactions and is represented by the slope of the log-linear relationship between mole fraction solubility and f_s which is the volume fraction of cosolvents and α is related to solute-soil and solvent-soil interactions via liquid and organic carbon phase activity coefficients [19, 23].

Statistical average of the volume based adsorption coefficients K_D was determined by the

relation;

$$K_D = \frac{\sum x/m \cdot Ce}{\sum (Ce)^2} \quad \ldots.(2)$$

where Ce is the equilibrium concentration of the solute in the liquid phase (μgm/ml) and x/m is the equilibrium concentration of the solute in the soil phase (μgm/gm) respectively and values are given in table 3.18.

The mole-based equilibrium adsorption partition coefficient (K_{mi}) values were determined by the equation

$$K_{mi} = K_{Di} / V_i \quad \ldots.(3)$$

where V_i is the molar volume of the liquid phase (ml/mol).

This theory is important for two reasons;

1. The theory enables prediction of adsorption of organic solute from a specified mixture of water and miscible organic solvents. This has implication on understanding the fate and transport of organic contaminants in real world,

complex waste streams such as industrial waste and land fill leachates.

2. This theory can be utilised to estimate the partition coefficient for adsorption from aqueous solution by plotting a graph between K_{Di} versus f_s and extrapolating to $f_s = 0$.

This theory is particularly important because it is very difficult to determine the adsorption coefficient of highly hydrophobic compounds from water.

The adsorption isotherms of endosulphan by soils at different f_s values in methanol-water and acetone-water mixtures, are plotted in Figs. 3.1 and 3.2 respectively; for the two soils and indicate the amount of endosulphan adsorbed (μgm/gm) by the soil.

According to the classification of Giles 1960 [24], the isotherms in both the systems are S-shaped and suggest that adsorption enhances at higher concentrations. The isotherms also suggest that the adsorption was probably due to marked localisation of forces of attraction over the >S ═ O group of endosulphan leading to interaction with soil sites.

These isotherms also show that endosulphan adsorption was higher on sandy loam soil than silt clay loam soil at all f_s values in both methanol-water and acetone-water systems. The higher adsorption on sandy loam soil in both the cosolvents may be due to greater amount of organic matter and other variations in soil properties.

On comparison (Figs. 3.1-3.2) the isotherms clearly show that endosulphan adsorption was higher in acetone-water system than methanol-water system at all f_s values. These isotherms also show that the endosulphan adsorption decreases with increase in f_s values in both the cosolvent systems. The lower adsorption at high f_s values was due to the increased solubility of endosulphan due to the presence of cosolvents in aqueous phase [23]. Due to this reason endosulphan affinity for soils is lower in presence of cosolvents and affinity of endosulphan for soils decreases at increasing rate of cosolvents in mixtures.

In both the cosolvent systems adsorption was in close agreement with Freundlich equation (Figs. 3.3-3.6).

$$x/m = K\, Ce^{1/n}$$

where K and 1/n are constants depending on the nature of endosulphan, soils and cosolvents of the system. In all cases the coefficient of determination (r^2) values (table 3.18) were greater than 0.95. The values of K and 1/n for soil-endosulphan combinations were estimated by least-squares fit to the adsorption isotherm. The values obtained are summarised in table 3.18. K is the Freundlich adsorption constant. The magnitude of K expresses the relative adsorption capacity for the adsorbate [25] for systems having comparable 1/n values and extent or degree of adsorption [26]. The value of 1/n provides an idea of intensity of adsorption which varies with the nature of the adsorbate for a given adsorbent. The value of 1/n also indicates the degree of linearity ($1/n < 1$) between solution equilibrium concentration and adsorption. The K values for methanol-water and acetone-water mixtures confirms the above order of adsorption and these values also confirms that addition of cosolvents to system reduces endosulphan adsorption by soils as proved by decrease in K values. The results are in agreement with the theoretical approach proposed by Rao et al. 1985 [19] quantifying the adsorption and transport of hydrophobic organic

chemicals from aqueous and aqueous-solvent mixtures. They found that adsorption coefficients from aqueous organic binary solvent mixtures decreases exponentially as f_s increases. The higher value of K at all f_s values in acetone-water mixtures than methanol-water mixtures confirms that endosulphan adsorption was higher in acetone-water mixtures than methanol-water mixtures. The lower adsorption in methanol-water mixtures in comparison to acetone-water mixtures at all f_s values may be due to the hydrogen bonding between alcoholic group (OH) of methanol and the sulphoxide group (> S ⟹ O) of endosulphan which is an electron donating group while that of acetone have dipole-dipole interactions with endosulphan. These two mechanisms of interaction could explain the less adsorption of endosulphan in methanol-water mixtures than acetone-water mixtures. The decrease in K values with increase in f_s values in both cosolvent mixtures also confirms that endosulphan adsorption decreases with increase in f_s values. The values of Freundlich exponent 1/n which is less than 1 (table 3.18) also suggests that isotherms were linear thereby indicating the dependence of endosulphan adsorption coefficients on the fractions of methanol and acetone in binary mixtures.

The affinity of endosulphan adsorption towards organic matter and clay content of soils was evaluated by calculating the K_{om} and K_c values as proposed by Grestl 1984 [27] and values so obtained are summarised in table 3.18. Silt clay loam soil had higher K_{om} values than sandy loam soil which is the case of low organic matter. Hamaker and Thompson 1972 [28], proposed that this tendency is due to the fact that organic matter may be responsible for making a significant contribution to the adsorption. The present study in both the cosolvent systems shows that endosulphan adsorption was attributed to organic matter which gave high K_{om} values. The results are in accordance with the work of Wahid and Sethunathan 1978 [29] who demonstrated that beyond 2% organic matter in soils the adsorption of parathion takes place almost entirely on the organic surfaces, but at organic matter level below 2% adsorption was significant on clay surfaces or inorganic surfaces.

Statistical average of K_D values for both the cosolvent mixtures was evaluated by equation (2) and values so obtained are summarised in table 3.18. Higher K_D values for sandy loam soil followed by silt clay loam soil also confirms that endosulphan

adsorption decreases with increase in f_s values for both the cosolvent systems.

Verification of Cosolvent theory :

The selected properties of methanol-water mixtures such as volume fraction of methanol (f_s), mass fraction of methanol (f_m) and mole fraction of methanol were evaluated by the following relations;

$$f_s = \frac{V_m}{V_m + V_w} \qquad \ldots.(5)$$

$$f_m = \left[1 + (P_w/P_m)\ \frac{(1 - f_s)}{f_s}\right]^{-1} \qquad \ldots.(6)$$

$$f_{mol} = \left[1 + \left(\frac{P_w \cdot M_m}{P_m \cdot M_w}\right)\ \frac{(1 - f_s)}{f_s}\right]^{-1} \qquad \ldots.(7)$$

where V_m, V_w are the volumes; P_m, P_w are the densities and M_m, M_w are the molecular weights of methanol (m) and water (w) respectively. Liquid densities (P_{mix}/ml) are based on f_m and data for 20°C were taken from table 3.111 of Chemical Engineer's Handbook by Perry and Chilton 1973 [30]. The molar volume V(ml/mol) were evaluated from the equation

$$V = [(1/P_{mix})\ (M_m\ f_{mol} + M_w\ (1 - f_{mol}))] \qquad \ldots.(8)$$

The values are summarised in table 3.19. Similar equations were used to evaluate the above properties in acetone-water mixtures using volume, density and molecular weight of acetone in place of methanol. The values are summarised in table 3.19.

Adsorption isotherm data such as K_D, K_m, K_{moc} and $LogK_{moc}$ used to evaluate the cosolvent theory are summarised in table 3.20. The K_m values were determined by dividing K_D values by liquid phase molar volume V (ml/mole). K_m values were normalised on organic carbon fraction (f_{oc}) of the respective soils giving K_{moc} values. Linear regression of the combined $LogK_{moc}$ data for soils yields equation at 20°C as

$$LogK_{moc} = -1.44\ f_s + 2.98 \qquad ....(9)$$

for acetone-water mixtures and

$$LogK_{moc} = -1.04\ f_s + 2.46 \qquad ....(10)$$

for methanol - water mixtures, by plotting $LogK_{moc}$ versus f_s. On the basis of this data for endosulphan adsorption on soils values of $LogK_{moc}$ are well

described by a single line over the entire range of f_s studies in both cosolvent systems. These data show that the cosolvent theory applies to endosulphan adsorption as has been observed for adsorption of other solutes from methanol-water and acetone-water mixtures. The data of both systems collapse on to a single line (Fig. 3.7) when normalised on f_{oc} as would be expected according to cosolvent theory [19].

Extrapolated estimate of aqueous phase partition coefficient :

The intercept values 2.98 and 2.46 in equations (9) and (10) are equal to the logarithm of the aqueous phase partition coefficient (K_{Dw} mol/gm) values for endosulphan obtained from the adsorption data of acetone-water and methanol-water mixtures respectively. The values of slopes 1.04 and 1.44 for methanol-water and acetone-water mixtures corresponds to the term $-\alpha\sigma_s$ of equation (1). The values of slope in Fig. 3.7 represents the combined effect of both α and σ_s. The term σ_s represents the effect of acetone and methanol on increase of endosulphan solubility. The values of σ_s corresponds to the slopes of the log-linear relationship between mole

fraction solubilities and volume fractions of methanol and acetone, f_s were calculated as was proposed by Fu and Luthy [23] by using the solubilities 330,000 µgm/ml, 110,000 µgm/ml and 0.325 µgm/ml of endosulphan in acetone, methanol and cosolvents free water respectively. The apparent value of α was evaluated by dividing $\alpha\sigma_s$ by σ_s and comes out to be 0.692 and 0.896 for acetone-water and methanol-water mixtures respectively. In both the cosolvents the α values were less than unity and suggest that perhaps acetone and methanol cosolvents-soil interactions were responsible for more effective adsorption at high f_s. The less value of α in acetone-water mixtures as compared to methanol-water mixtures speculate that acetone expanded the soil organic matter matrix greater than methanol resulting in the increased accessibility of endosulphan to the soil organic matter. The manner in which this phenomena impacts the adsorption of endosulphan to soils in presence of cosolvents (acetone, methanol) is an issue for further study.

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CHAPTER IV

EFFECT OF RELEVANT FACTORS ON THE SORPTION OF PESTICIDES, ENDOSULPHAN ON TWO INDIAN SOILS - THE NATURAL ION EXCHANGERS

IV.1 INTRODUCTION

Pesticides are carcinogenic and mutagenic substances, yet they are indispensable in modern agriculture because of their extensive use for crop production measures. They possess an accumulating tendency as well as a persistent nature. Their concentration in air, water, soil flora and fauna is increasing day by day owing to their repeated and indiscriminate use in agriculture. To meet the world wide problem of environmental protection and pollution control, it is necessary to detect, separate, identify and determine, pesticide residues in our ecosystem and then to take proper steps for their removal. The adsorption of pesticides on soils has been a significant feature. The frequent detection of pesticides in surface and groundwater has greatly increased the experimental studies on pesticide adsorption by soils [1-3].

Most of the data on pesticide adsorption by soils deal with aqueous solutions [4-11]. However, in natural environment it is likely that pesticide adsorption on soils could occur in a mixture of water and organic solvents. Several workers [12-14] have focused on adsorption of certain pesticides from

non-aqueous solvents and solvent mixtures. Recently: Rawat et al. [15], Singh and Singh [16] have studied the influence of organic solvents methanol and acetone on endosulphan adsorption and have reported that when f_s (volume fraction of organic solvent) increases adsorption of endosulphan on different soils decreases.

In the present investigation an attempt has been made to study the effect of different factors such as exchangeable ions, organic matter, temperature and surfactants on the adsorption of endosulphan at 0.25 f_s value and to relate the Freundlich constants and distribution coefficients to various soil properties. Thermodynamic properties were also evaluated for the interaction of endosulphan with soil.

IV.2 EXPERIMENTAL

IV.2.1 Collection of Soil Samples : The surface soil samples (0-30 cms.) of sandy loam (Mukteshwar) and silt clay loam (Bhopal) soils were collected from Mukteshwar district of Uttar Pradesh and Bhopal district of Madhya Pradesh, India; respectively. The soils were dried, crushed and sieved to obtain samples with a small and nearly homogeneous particle size. The physico-chemical properties of the soils were determined by the standard techniques as mentioned in the experimental portion of chapter II of this thesis and values are summarized in Table 4.1.

IV.2.2 Reagents : Endosulphan was obtained from Indo-Gulf Fertilizers and Chemicals Corporation Ltd., Sultanpur (U.P.). All other chemicals and reagents used were of analytical reagent grade.

IV.2.3 Apparatus : An electric temperature controlled SICO shaker was used for shaking; an Elico pH meter model Li-10 was used for pH measurements; Beckmann model L3-50 ultracentrifuge was used for centrifugation; a systronic conductivity meter dip

type cell for electrical conductance measurements and Bausch and Lomb spectrophotometer model spectronic 20 for spectrophotometric work.

IV.2.4 Preparation of Sodium Saturated Soil : Sodium saturated soil was prepared vide Aldrich and Buchanan's method [17]. The natural soil was broken up in a mortar using a pestle and was diluted with distilled water. The soil was dispersed by electrical stirring and than treated with 1.0N NaCl. The mixture was shaken for about one hour, after which the supernatant acid salt solution was removed from the soil suspension by decantation The soil suspension was than filtered through a Buchner funnel and washed with distilled water till the filtrate becomes free from chloride ions. The soil was transferred from the funnel and used for adsorption studies.

IV.2.5 Preparation of Hydrogen Saturated Soil : Hydrogen soil was freshly prepared vide Aldrich and Buchanan's method [17] in a similar manner as the sodium soil. The natural soil was treated with 1.0N HCl to convert it in hydrogen form and than washed with distilled water to make it free from chloride ions. The soil was than used for adsorption studies.

IV.2.6 Preparation of Organic Matter Removed Soil : Organic matter was removed from the soils using the Black method [18]. In this method natural soil was treated with 30% H_2O_2 to remove organic matter. The organic matter removed soil was than passed through a 60 mesh sieve, dried and stored in a vacuum desiccator on P_2O_5.

These soils were used as adsorbents for studying the effect of exchangeable ions (H^+ and Na^+) and organic matter on endosulphan adsorption.

The effects of anionic surfactant (sodium dodecyl sulphate), non-ionic surfactant (Tween-20) and temperature on endosulphan adsorption were studied using natural soils as adsorbents.

IV.2.7 Adsorption Studies : The adsorption of Endosulphan on Natural soils, Soils from which organic matter had been removed, Hydrogen saturated soil and Sodium saturated soil was analyzed by the batch technique. Studies, as already mentioned, were performed at 0.25 f_s (volume fraction of cosolvent) value by taking eight concentrations of endosulphan (100, 200, 300, 400, 500, 600, 800, 1000 µgm/ml)

solutions in different flasks and the volume adjusted to 20 ml with distilled water. To these solutions one gram of each type of soil was added and suspensions were kept at 20°C in an incubator shaker where it was shaken for 3 hrs and then kept without shaking for 24 hrs. The suspensions were centrifuged at 10,000 rpm for 10 minutes using a Bekmann Model L3-50 ultracentrifuge and the supernatants were collected. The amount of endosulphan present in supernatant was estimated spectrophotometrically [19] to calculate the amount of endosulphan adsorbed. The experiments were conducted in duplicate and each isotherm determination consisted of sixteen flasks for each of eight endosulphan dose and one blank flask containing soil and no endosulphan.

The effects of anionic (sodium dodecyl sulphate) and non-ionic (Tween-20) surfactants on endosulphan adsorption on natural soils from both sites were studied using the same procedure with the addition of 5ml of 0.1% surfactant solution in each

flask before making up the volume to 20ml with distilled water.

To study the effect of temperature, other than 20°C; suspensions prepared as above were shaken at 10°C and 40°C respectively, using natural soils as adsorbents.

The distribution coefficient (Kd) statistical values for both the soils for all treatments/effects were calculated by using the equation

$$Kd = \frac{\sum x/m \cdot Ce}{\sum (Ce)^2} \qquad \ldots.(1)$$

where x/m is the amount of endosulphan adsorbed per gram of soil and Ce is the amount of endosulphan in equilibrium suspension per ml.

IV.3 RESULTS

The two soils varied widely in their composition and physico-chemical properties which are summarized in table 4.1.

The adsorption isotherms are presented in Figs. 4.1-4.2 and the adsorption data are summarized in tables 4.2-4.17. The adsorption data was fitted to the Freundlich isotherms which are shown in Figs. 4.3-4.4 and Freundlich constants (K and 1/n) are given in tables 4.24, 4.25.

Plots of $\ln \frac{Cs}{Ce}$ versus Cs, Figs. 4.5-4.6 , for the two soils were drawn for evaluating the thermodynamic equilibrium constant (Ko), (table 4.26). The values of Cs and $\ln \frac{Cs}{Ce}$ are summarized in tables 4.18-4.23 for the two soils for different temperatures. K_o, was estimated by least squares fit.

Standard enthalpy change ($\Delta H°$) was determined from the slope of the plot between lnKo and 1/T (Fig. 4.7). Values for thermodynamic parameters are presented in table 4.26.

Table 4.1

Composition and Physico-chemical properties of the soils

Properties	Sandy loam soil (Mukteshwar)	Silt clay loam soil (Bhopal)
% Sand	59.12	14.85
% Silt	34.80	49.15
% Clay	6.0	36.0
Texture	Sandy loam	Silt clay loam
pH	6.0	8.5
Electrical conductance (S m^{-1})	2.833×10^{-4}	4.32×10^{-4}
% Organic matter	4.06002	0.98268
% Organic carbon	2.355	0.57
Cation Exchange Capacity [C mol P^{+} Kg^{-1}]	17.0	23.80
Bulk Density (gm/cm^3)	1.18	1.38
% $CaCO_3$	4.75	4.60
Surface Area (m^2/gm)	58.979	240.96
Porosity	0.33	0.43

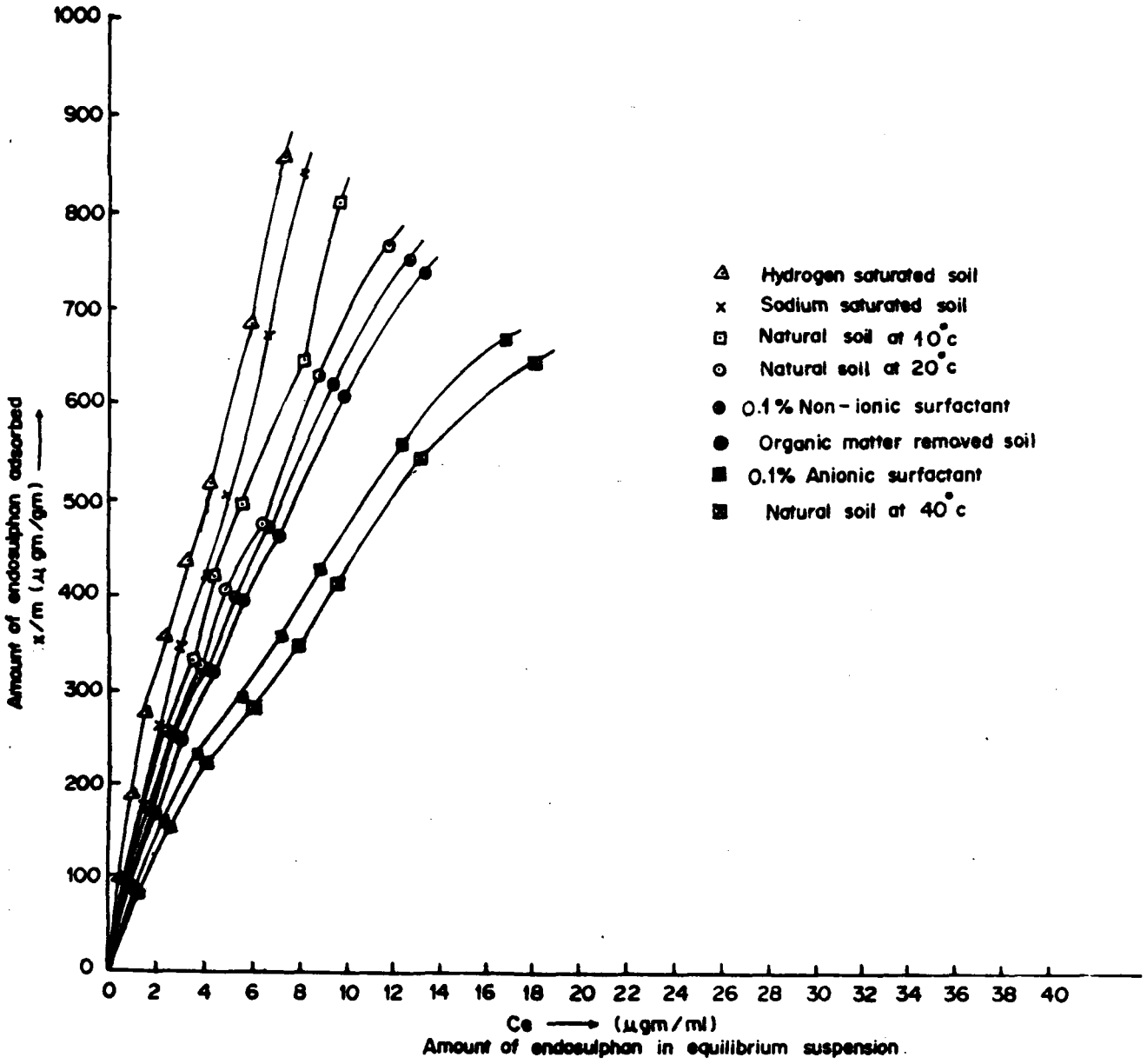


Fig. 4.1: Adsorption isotherms of endosulphan on different forms of sandy loam soil.

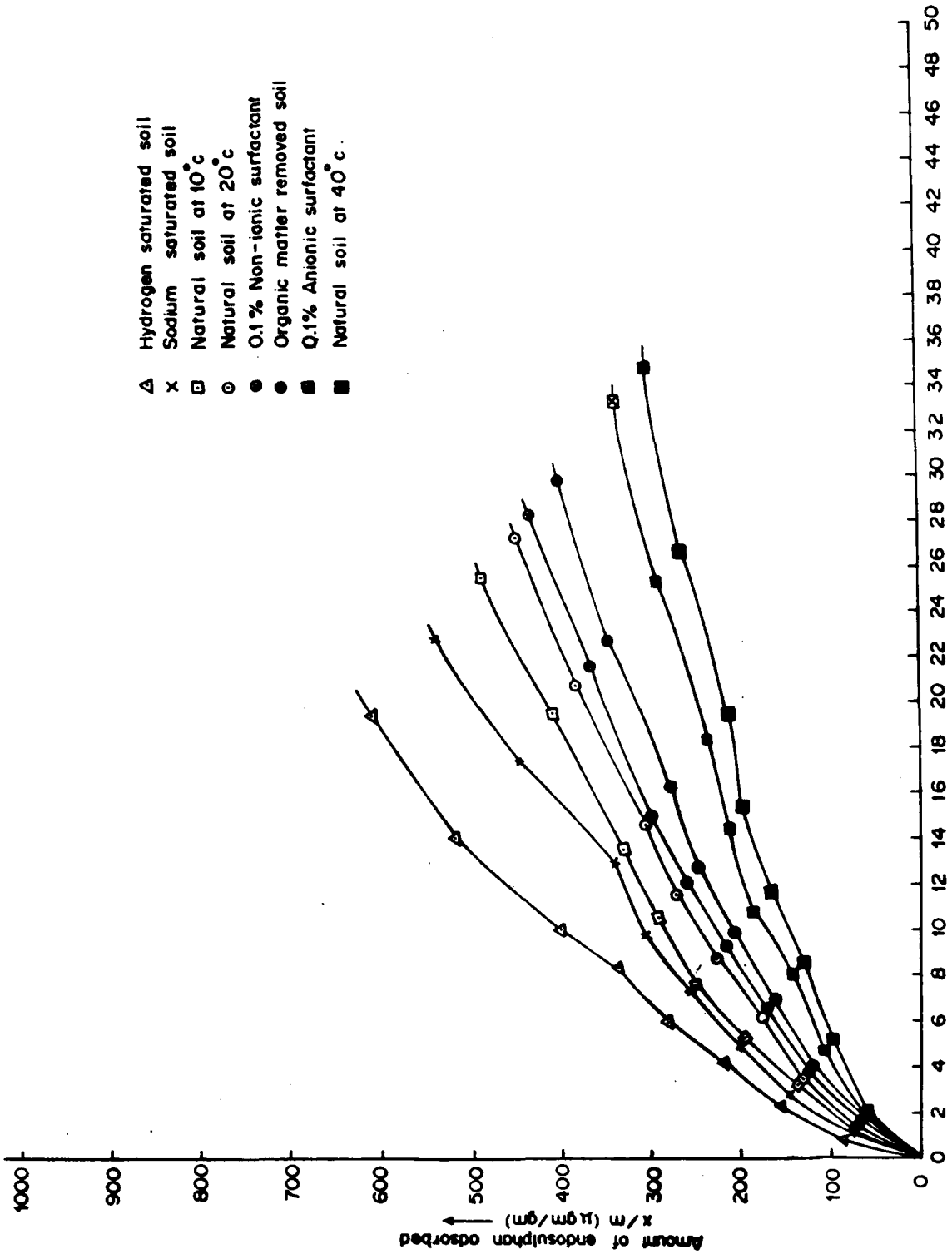


Fig. 4.2 : Adsorption isotherms of endosulphan on different forms of silt clay loam soil

Table 4.2

Adsorption of Endosulphan on Hydrogen saturated Sandy loam (Mukteshwar) soil in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	8	92	0.4	-0.3979	1.9637	230.000	
200	18	182	0.9	-0.0457	2.2600	202.222	
300	28	272	1.4	0.1461	2.4345	194.285	
400	46	354	2.3	0.3617	2.5490	153.913	122.512
500	64	436	3.2	0.5051	2.6394	136.250	
600	84	516	4.2	0.6232	2.7126	122.857	
800	118	682	5.9	0.7708	2.8337	115.593	
1000	146	854	7.3	0.8633	2.9314	116.986	

Table 4.3

Adsorption of Endosulphan on Sodium saturated Sandy loam (Mukteshwar) soil in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	10	90	0.5	-0.3010	1.9542	180.000	
200	26	174	1.3	0.1139	2.2405	133.846	
300	40	260	2.0	0.3010	2.4149	130.000	
400	58	342	2.9	0.4623	2.5340	117.931	105.581
500	80	420	4.0	0.6020	2.6232	105.000	
600	96	504	4.8	0.6812	2.7024	105.000	
800	130	670	6.5	0.8129	2.8260	103.077	
1000	162	838	8.1	0.9084	2.9232	103.456	

Table 4.4

Adsorption of Endosulphan on Natural Sandy loam

(Mukteshwar) soil at 10°C in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	11	89	0.55	-0.2596	1.9494	161.818	
200	28	172	1.40	0.1461	2.2355	122.857	
300	46	254	2.30	0.3617	2.4048	110.435	
400	70	330	3.50	0.5440	2.5185	94.286	86.197
500	82	418	4.10	0.6127	2.6211	101.951	
600	110	490	5.50	0.7403	2.6901	89.091	
800	162	638	8.10	0.9084	2.8048	78.765	
1000	192	808	9.60	0.9822	2.9074	84.167	

Table 4.5

Adsorption of Endosulphan on Natural Sandy loam (Mukteshwar) soil at 20°C in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	12	88	0.6	-0.2218	1.9444	146.666	
200	32	168	1.6	0.2041	2.2253	105.000	
300	48	252	2.4	0.3802	2.4014	105.000	
400	76	324	3.8	0.5797	2.5105	85.263	71.550
500	96	404	4.8	0.6812	2.6063	84.166	
600	128	472	6.4	0.8061	2.6739	73.750	
800	176	624	8.8	0.9441	2.7951	70.909	
1000	234	766	11.7	1.0681	2.8842	65.407	

Table 4.6

Adsorption of Endosulphan on Natural Sandy loam (Mukteshwar) soil at 40°C in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	22	78	1.1	0.0413	1.8920	70.909	
200	50	150	2.5	0.3979	2.1760	60.000	
300	80	220	4.0	0.6020	2.3424	55.000	
400	120	280	6.0	0.7781	2.4471	46.666	39.933
500	158	342	7.9	0.8976	2.5340	43.291	
600	190	410	9.5	0.9777	2.6127	43.157	
800	260	540	13.0	1.1139	2.7323	41.538	
1000	360	640	18.0	1.2552	2.8061	35.555	

Table 4.7

Adsorption of Endosulphan on Organic matter removed Sandy loam (Mukteshwar) soil in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	14	86	0.7	-0.1549	1.9344	122.857	
200	38	162	1.9	0.2787	2.2095	85.263	
300	58	242	2.9	0.4623	2.3838	83.448	
400	86	314	4.3	0.6334	2.4969	73.023	61.099
500	110	390	5.5	0.7403	2.5910	70.909	
600	142	458	7.1	0.8512	2.6608	64.507	
800	196	604	9.8	0.9912	2.7810	61.632	
1000	266	734	13.3	1.1238	2.8656	55.187	

Table 4.8

Adsorption of Endosulphan on Sandy loam (Mukteshwar) soil in presence of 0.1% non-ionic surfactant in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	14	86	0.7	-0.1549	1.9344	122.857	
200	32	168	1.6	0.2041	2.2253	105.000	
300	52	248	2.6	0.4149	2.3944	95.385	
400	84	316	4.2	0.6232	2.4996	75.238	65.552
500	104	396	5.2	0.7160	2.5976	76.154	
600	132	468	6.6	0.8195	2.6702	70.909	
800	188	612	9.4	0.9731	2.7867	65.106	
1000	252	748	12.6	1.1003	2.8739	59.365	

Table 4.9

Adsorption of Endosulphan on Sandy loam (Mukteshwar) soil in presence of 0.1% anionic surfactant in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	18	82	0.9	-0.0458	1.9138	91.111	
200	44	156	2.2	0.3424	2.1931	70.909	
300	72	228	3.6	0.5563	2.3579	63.333	
400	110	290	5.5	0.7403	2.4623	52.727	44.427
500	144	356	7.2	0.8573	2.5514	49.444	
600	176	424	8.8	0.9444	2.6273	48.182	
800	244	556	12.2	1.0863	2.7450	45.573	
1000	336	664	16.8	1.2253	2.8221	39.524	

Table 4.10

Adsorption of Endosulphan on Hydrogen saturated Silt clay loam (Bhopal) soil in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	16	84	0.8	-0.0969	1.9242	105.000	
200	46	154	2.3	0.3617	2.1875	66.956	
300	84	216	4.2	0.6232	2.3344	51.428	
400	120	280	6.0	0.7781	2.4471	46.666	35.688
500	168	332	8.4	0.9242	2.5211	39.523	
600	200	400	10.0	1.0000	2.6020	40.000	
800	282	518	14.1	1.1492	2.7143	36.737	
1000	392	608	19.6	1.2922	2.7839	31.020	

Table 4.11

Adsorption of Endosulphan on Sodium saturated Silt clay loam (Bhopal) soil in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	22	78	1.1	0.0413	1.8920	70.909	
200	56	144	2.8	0.4471	2.1583	51.429	
300	100	200	5.0	0.6989	2.3010	40.000	
400	146	254	7.3	0.8633	2.4048	34.795	26.133
500	196	304	9.8	0.9912	2.4828	31.020	
600	260	340	13.0	1.1139	2.5314	26.154	
800	350	450	17.5	1.2430	2.6532	25.714	
1000	460	540	23.0	1.3617	2.7323	23.478	

Table 4.12

Adsorption of Endosulphan on Natural Silt clay loam (Bhopal) soil at 10°C in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	26	74	1.3	0.1139	1.8693	56.923	
200	64	136	3.2	0.5051	2.1335	42.500	
300	106	194	5.3	0.7242	2.2878	36.604	
400	152	248	7.6	0.8808	2.3944	32.632	21.905
500	210	290	10.5	1.0212	2.4623	27.619	
600	270	330	13.5	1.1303	2.5185	24.444	
800	392	408	19.6	1.2922	2.6106	20.816	
1000	514	486	25.7	1.4099	2.6866	18.911	

Table 4.13

Adsorption of Endosulphan on Natural Silt clay loam (Bhopal) soil at 20°C in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F}.\frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	28	72	1.4	0.1461	1.8573	51.428	
200	70	130	3.5	0.5440	2.1139	37.142	
300	124	176	6.2	0.7923	2.2455	28.387	
400	176	224	8.8	0.9444	2.3502	25.454	18.869
500	232	268	11.6	1.0644	2.4281	23.103	
600	294	306	14.7	1.1673	2.4857	20.816	
800	418	382	20.9	1.3201	2.5820	18.277	
1000	550	450	27.5	1.4393	2.6532	16.363	

Table 4.14

Adsorption of Endosulphan on Natural Silt clay loam (Bhopal) soil at 40°C in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	40	60	2.0	0.3222	1.7634	30.000	
200	102	98	5.1	0.7075	1.9912	19.215	
300	170	130	8.5	0.9294	2.1139	15.294	
400	234	166	11.7	1.0681	2.2201	14.188	10.134
500	302	192	15.4	1.1875	2.2833	12.467	
600	390	210	19.5	1.2900	2.3222	10.769	
800	534	266	26.7	1.4265	2.4248	9.962	
1000	700	300	35.0	1.5440	2.4771	8.571	

Tale 4.15

Adsorption of Endosulphan on Organic matter removed Silt clay loam (Bhopal) soil in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	34	66	1.7	0.2304	1.8195	38.823	
200	82	118	4.1	0.6127	2.0718	28.780	
300	140	160	7.0	0.8450	2.2041	22.857	
400	198	202	9.9	0.9956	2.3053	20.404	15.449
500	256	244	12.8	1.1072	2.3873	19.062	
600	326	274	16.3	1.2121	2.4377	16.089	
800	456	344	22.8	1.3579	2.5365	15.087	
1000	600	400	30.0	1.4771	2.6020	13.333	

Table 4.16

Adsorption of Endosulphan on Silt clay loam (Bhopal) soil in presence of 0.1% non-ionic surfactant in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $KD = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	32	68	1.6	0.2041	1.8325	42.500	
200	76	124	3.8	0.5797	2.0934	32.632	
300	132	168	6.6	0.8195	2.2253	25.455	
400	186	214	9.3	0.9684	2.3304	23.011	17.517
500	242	258	12.1	1.0827	2.4116	21.322	
600	302	298	15.1	1.1789	2.4742	19.735	
800	434	366	21.7	1.3364	2.5634	16.866	
1000	568	432	28.4	1.4533	2.6354	15.211	

Table 4.17

Adsorption of Endosulphan on Silt clay loam (Bhopal) soil in presence of 0.1% anionic surfactant in methanol-water mixture

Amount of Endosulphan Added µgm/ml	Amount in equilibrium suspension Ce/20 ml	Amount Adsorbed by soil/gm x/m	Ce/ml	Log Ce	Log x/m	$Kd = \frac{I-F}{F} \cdot \frac{V}{W}$	Statistical Kd $Kd = \frac{\sum x/m.Ce}{\sum (Ce)^2}$
100	38	62	1.9	0.2787	1.7923	32.631	
200	94	106	4.7	0.6720	2.0253	22.553	
300	160	140	8.0	0.9030	2.1461	17.500	
400	216	184	10.8	1.0334	2.2648	17.037	11.711
500	290	210	14.5	1.1613	2.3222	14.482	
500	368	232	18.4	1.2648	2.3654	12.608	
800	510	290	25.5	1.4065	2.4623	11.372	
1000	668	332	33.4	1.5237	2.5211	9.940	

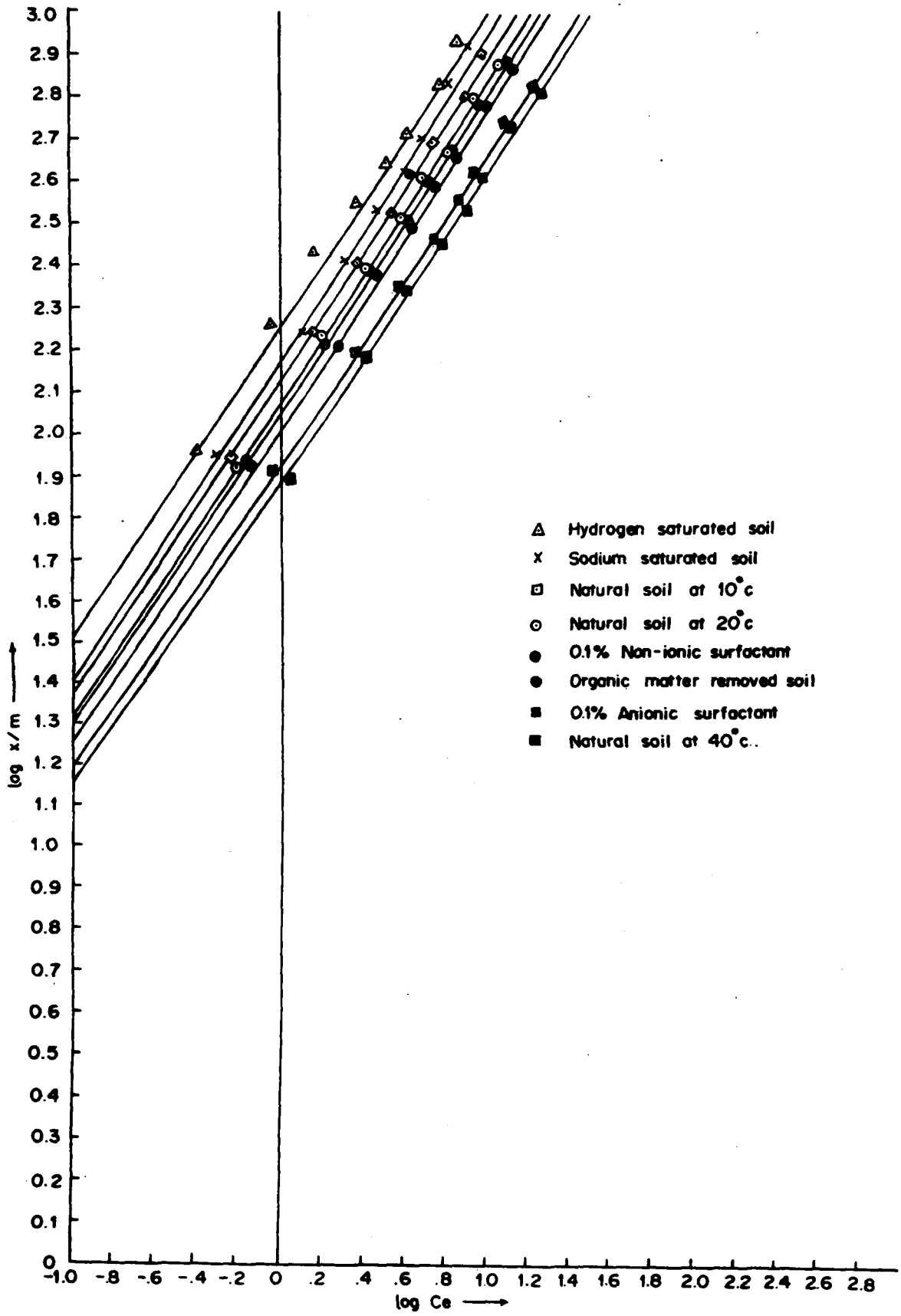


Fig. 4.3: Freundlich isotherms for adsorption of endosulphan on different forms of sandy loam soil.

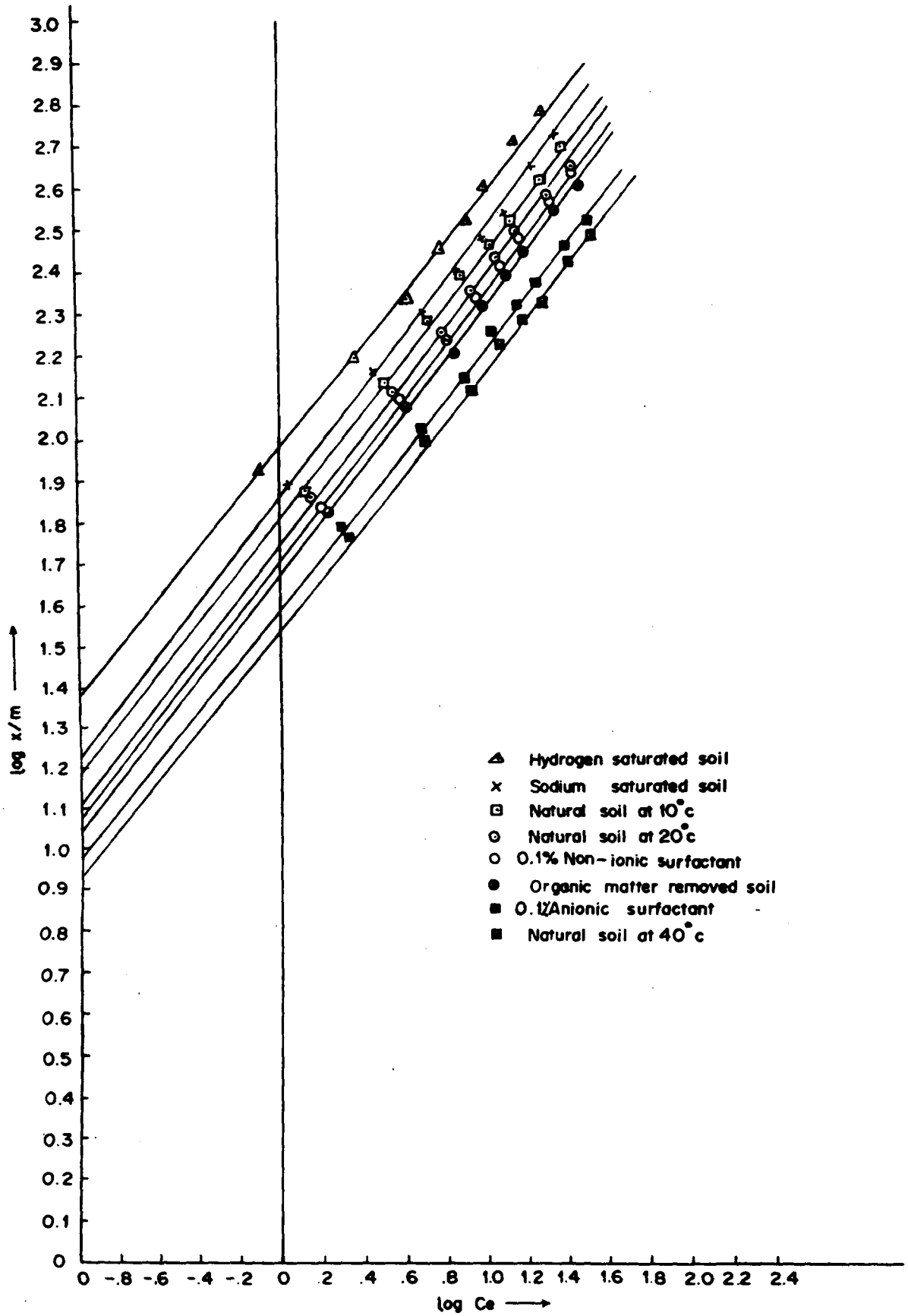


Fig. 4.4: Freundlich isotherms for adsorption of endosulphan on different forms of silt clay loam soil.

Table 4.18

Values of Cs, Cs/Ce, $\ln \frac{Cs}{Ce}$ for Natural Sandy loam (Mukteshwar) soil at 10°C

Amount of Endosulphan Added µgm/ml	Cs	Cs/Ce	$\ln \frac{Cs}{Ce}$
100	99.256	73431948	18.112
200	191.822	55751705	17.836
300	283.272	50114525	17.729
400	368.031	42786192	17.571
500	466.172	46264741	17.649
600	546.469	40428825	17.515
800	711.526	35743197	17.391
1000	901.118	38194241	17.458

Table 4.19

Values of Cs, Cs/Ce, ln $\frac{Cs}{Ce}$ for Natural Sandy loam (Mukteshwar) soil at 20°C

Adsorption of Endosulphan Added µgm/ml	Cs	Cs/Ce	ln $\frac{Cs}{Ce}$
100	98.141	66556296	18.013
200	187.361	47648260	17.679
300	281.415	47648158	17.679
400	361.339	38691820	17.471
500	450.558	38194240	17.458
600	526.395	33467231	17.326
800	695.912	32178045	17.286
1000	854.277	29709863	17.206

Table 4.20

Values of Cs, Cs/Ce, ln $\frac{Cs}{Ce}$ for Natural Sandy loam (Mukteshwar) soil at 40°C

Adsorption of Endosulphan Added µgm/ml	Cs	Cs/Ce	ln $\frac{Cs}{Ce}$
100	86.989	32178045	17.286
200	167.286	27227576	17.119
300	245.353	24958612	17.032
400	312.268	21177003	16.868
500	381.413	19645213	16.803
600	457.250	19584748	16.790
800	602.231	18849861	16.752
1000	713.756	16134860	16.596

Table 4.21

Values of Cs, Cs/Ce, ln $\frac{Cs}{Ce}$ for Natural

Silt clay loam (Bhopal) soil at 10°C

Adsorption of Endosulphan Added µgm/ml	Cs	Cs/Ce	ln $\frac{Cs}{Ce}$
100	20.200	6322641.8	15.659
200	37.124	4720620.9	15.367
300	52.957	4065706.8	15.218
400	67.697	3624501.3	15.103
500	79.163	3067742.4	14.936
600	90.082	2715128.3	14.814
800	111.373	2312141.0	14.653
1000	132.665	2100454.8	14.557

Table 4.22

Values of Cs, Cs/Ce, ln $\frac{Cs}{Ce}$ for Natural Silt clay loam (Bhopal) soil at 20°C

Adsorption of Endosulphan Added µgm/ml	Cs	Cs/Ce	ln $\frac{Cs}{Ce}$
100	19.654	5712347.8	15.558
200	35.486	4125584.8	15.232
300	48.043	3153052.3	14.963
400	61.146	2827323.7	14.854
500	73.157	2566179.2	14.757
600	83.530	2312140.9	14.653
800	104.276	2030146.0	14.523
1000	122.838	1817565.2	14.413

Table 4.23

Values of Cs, Cs/Ce, ln $\frac{Cs}{Ce}$ for Natural

Silt clay loam (Bhopal) soil at 40°C

Adsorption of Endosulphan Added µgm/ml	Cs	Cs/Ce	ln $\frac{Ce}{Ce}$
100	16.378	3332203.0	15.019
200	26.751	2134352.3	14.573
300	35.486	1698770.3	14.345
400	45.313	1575913.6	14.270
500	52.411	1384811.6	14.141
600	57.324	1196175.4	13.994
800	72.611	1106574.3	13.916
1000	81.892	952057.9	13.766

Table 4.24

Values of Freundlich Constants and Distribution Coefficients for the adsorption of Endosulphan on Sandy loam (Mukteshwar) soil

Soil	K	1/n	r^2	Regression Equation	Kd	K_{om}	K_c
Hydrogen saturated soil	181.970	0.750	0.9854	Y=181.970+0.75x	122.512		
Sodium saturated soil	151.356	0.750	0.9961	Y=151.356+0.75x	105.581		
Natural soil at 10°C	134.896	0.750	0.9903	Y=134.896+0.75x	86.197	2123.068	1436.62
Natural soil at 20°C	117.489	0.725	0.9852	Y=117.489+0.725x	71.550	1762.306	1192.50
Soil with 0.1% non-ionic surfactant	112.201	0.750	0.9843	Y=112.201+0.75x	65.552		
Organic matter removed soil	102.329	0.750	0.9859	Y=102.329+0.75x	61.099		
Soil with 0.1% anionic surfactant	85.113	0.725	0.9826	Y= 85.113+0.725x	44.427		
Natural soil at 40°C	77.624	0.725	0.9849	Y= 77.624+0.725x	39.933	983.566	665.55

Table 4.25

Values of Freundlich Constants and Distribution Coefficients for the adsorption of Endosulphan on Silt clay loam (Bhopal) soil

Soil	K	1/n	r^2	Regression Equation	Kd	K_{om}	K_c
Hydrogen saturated soil	95.499	0.625	0.9732	Y=95.499+0.625x	35.668		
Sodium saturated soil	72.443	0.625	0.9731	Y=72.443+0.625x	26.133		
Natural soil at 10°C	66.069	0.625	0.9578	Y=66.069+0.625x	21.904	2229.006	60.84
Natural soil at 20°C	56.234	0.625	0.9656	Y=56.234+0.625x	18.869	1920.157	52.41
Soil with 0.1% non-ionic surfactant	51.286	0.625	0.9684	Y=51.286+0.625x	17.517		
Organic matter removed soil	47.863	0.625	0.9670	Y=47.863+0.625x	15.449		
Soil with 0.1% anionic surfactant	38.904	0.625	0.9581	Y=38.904+0.625x	11.710		
Natural soil at 40°C	34.673	0.625	0.9586	Y=34.673+0.625x	10.134	1031.261	28.15

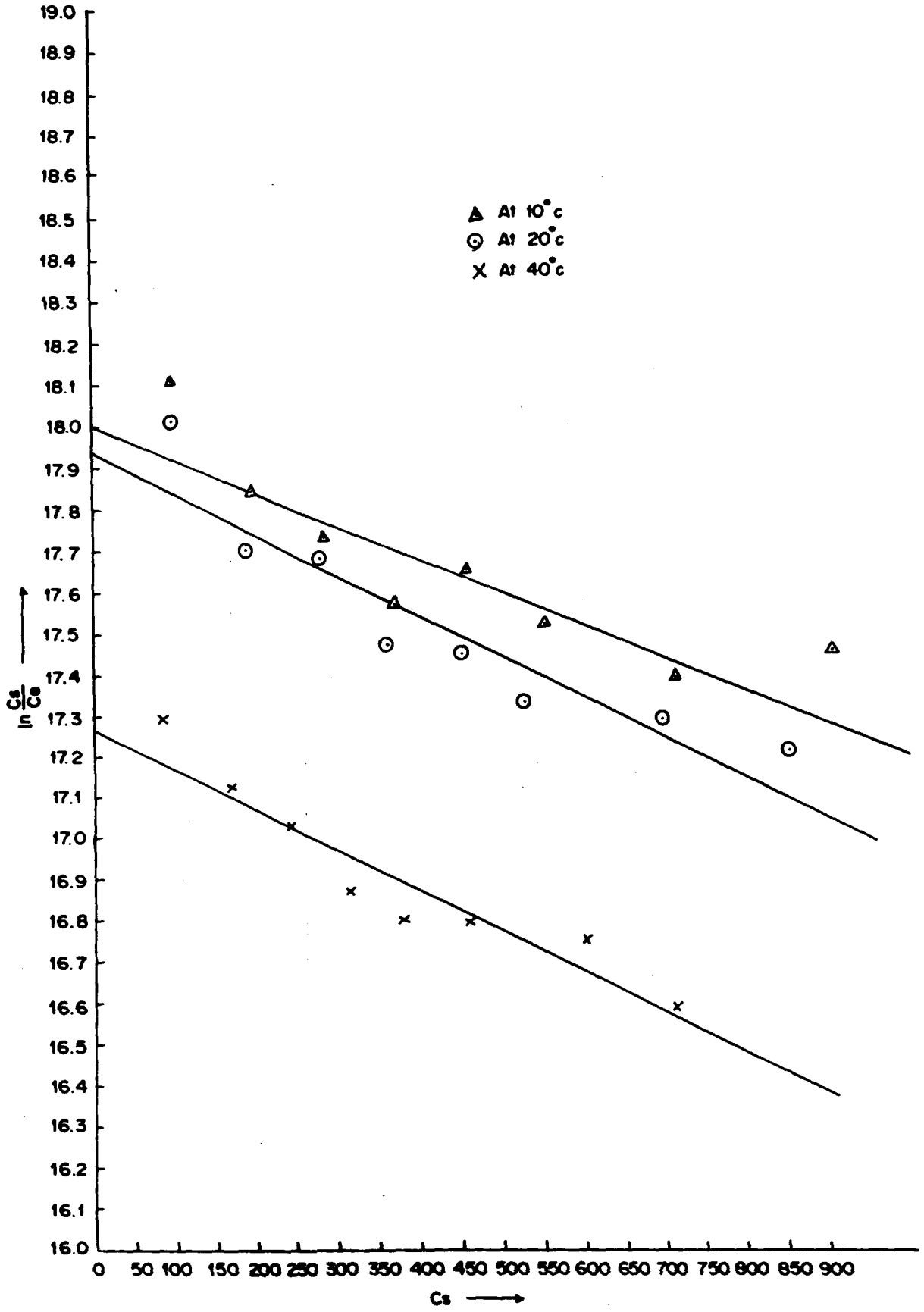


Fig. 4.5: Plots of $\ln \frac{Cs}{Ce}$ versus Cs for sandy loam soil at different temperatures.

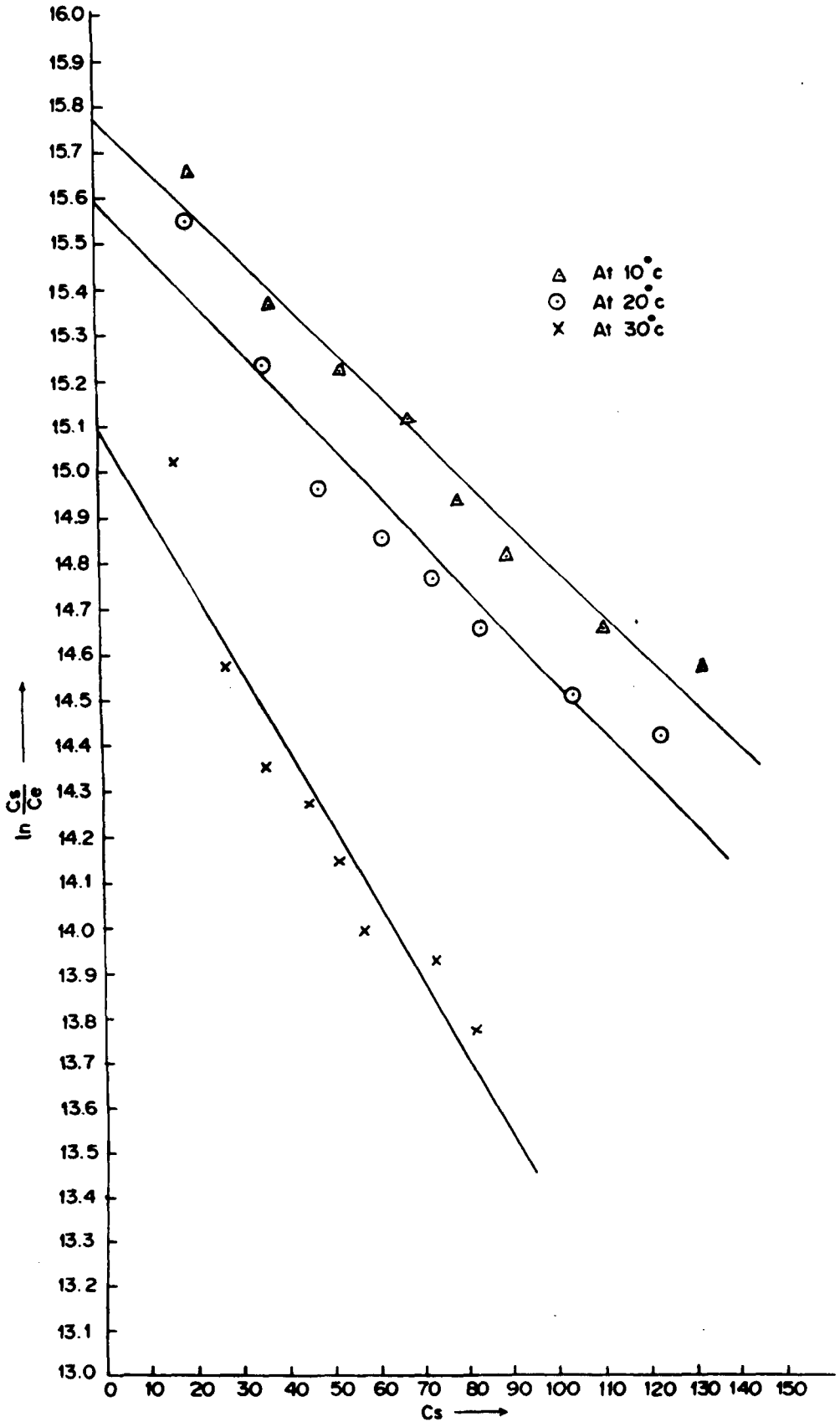


Fig. 4.6 : Plots of $\ln \frac{Cs}{Ce}$ versus Cs for silt clay loam soil at different temperatures.

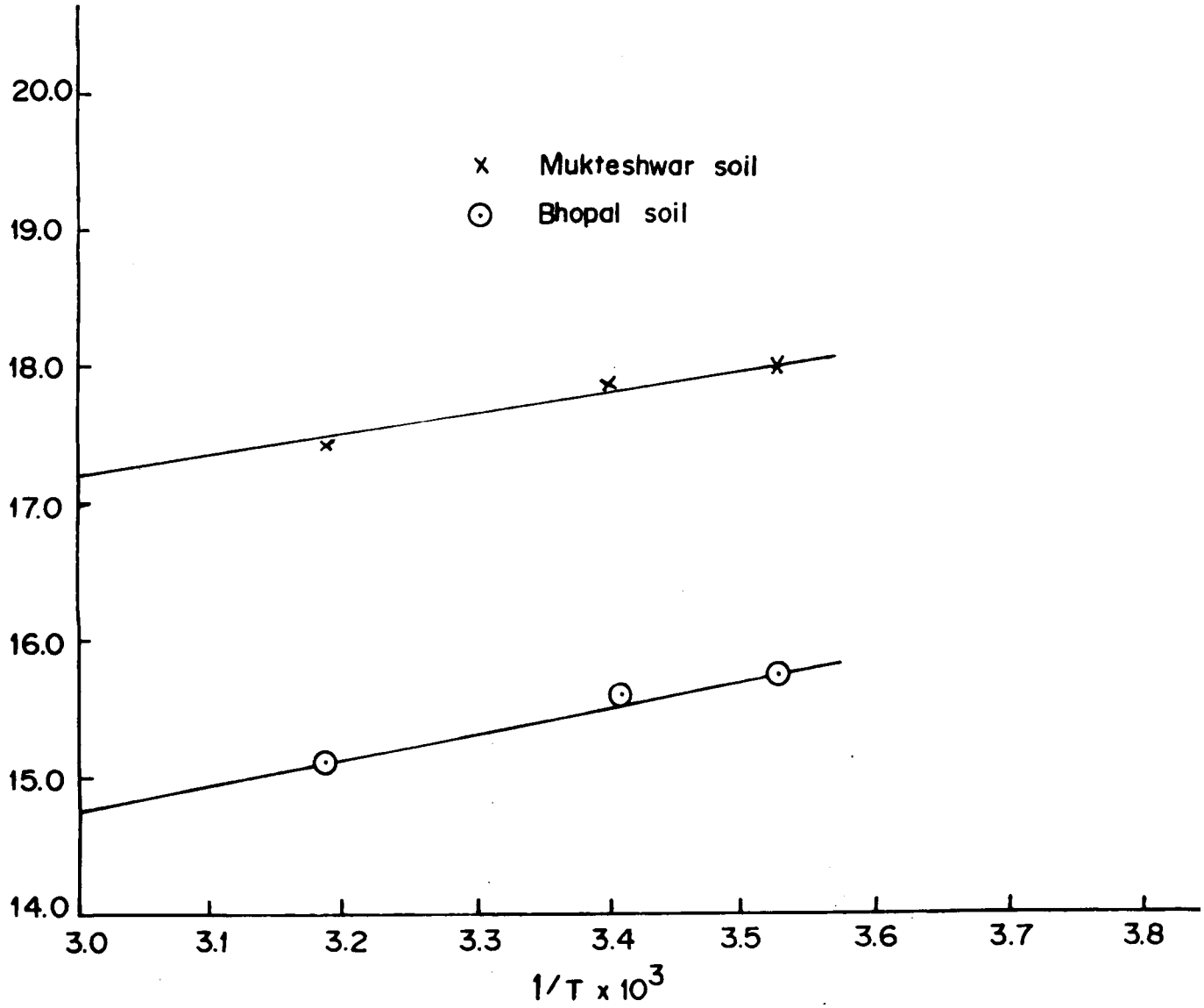


Fig. 4.7: Determination of enthalpy of adsorption for sandy loam and silt clay loam soil.

Table 4.26

Values of various Thermodynamic Parameters for the Adsorption of Endosulphan at Different Temperatures

Thermodynamic Parameter	Sandy Loam (Mukteshwar) soil			Silt Clay Loam (Bhopal) soil		
	10°C	20°C	40°C	10°C	20°C	40°C
Ko	6.5659×10^7	6.1836×10^7	3.1642×10^7	7.0603×10^6	5.8972×10^6	3.5768×10^6
$\triangle G°$ (KJ/mol)	-42.331	-43.680	-44.919	-37.086	-37.959	-39.249
$\triangle H°$ (KJ/mol)		-16.628			-15.388	
$\triangle S°$ (KJ/mol/°K)	0.0908	0.0923	0.0903	0.0766	0.0770	0.0762

IV.4 DISCUSSION

It is evident from table 4.1 that the two soils differed widely in their physico-chemical properties. Sandy loam (Mukteshwar) soil was rich in organic matter while the silt clay loam (Bhopal) soil was rich in clay.

Adsorption isotherms between the amount of endosulphan adsorbed (µgm/gm) on soil and the amount of endosulphan in equilibrium suspension (µgm/ml) are plotted in Figs. 4.1 and 4.2 and the adsorption data are given in tables 4.2-4.17. It is clear from these isotherms that endosulphan adsorption was higher on sandy loam (Mukteshwar) soil than on silt clay loam (Bhopal) soil. The isotherms (Figs. 4.1 and 4.2) for both the soils for all treatments/effects are S-shaped according to the classification of Giles et al. 1960 [22]. Endosulphan exhibited maximum affinity for Hydrogen saturated soils and minimum affinity at 40°C and adsorption follows the order :

Hydrogen saturated soil > Sodium saturated soil > Natural soil at 10°C > Natural soil at 20°C > Soil with 0.1% Non-ionic Surfactant > Soil from which organic matter was removed > Soil with 0.1% anionic

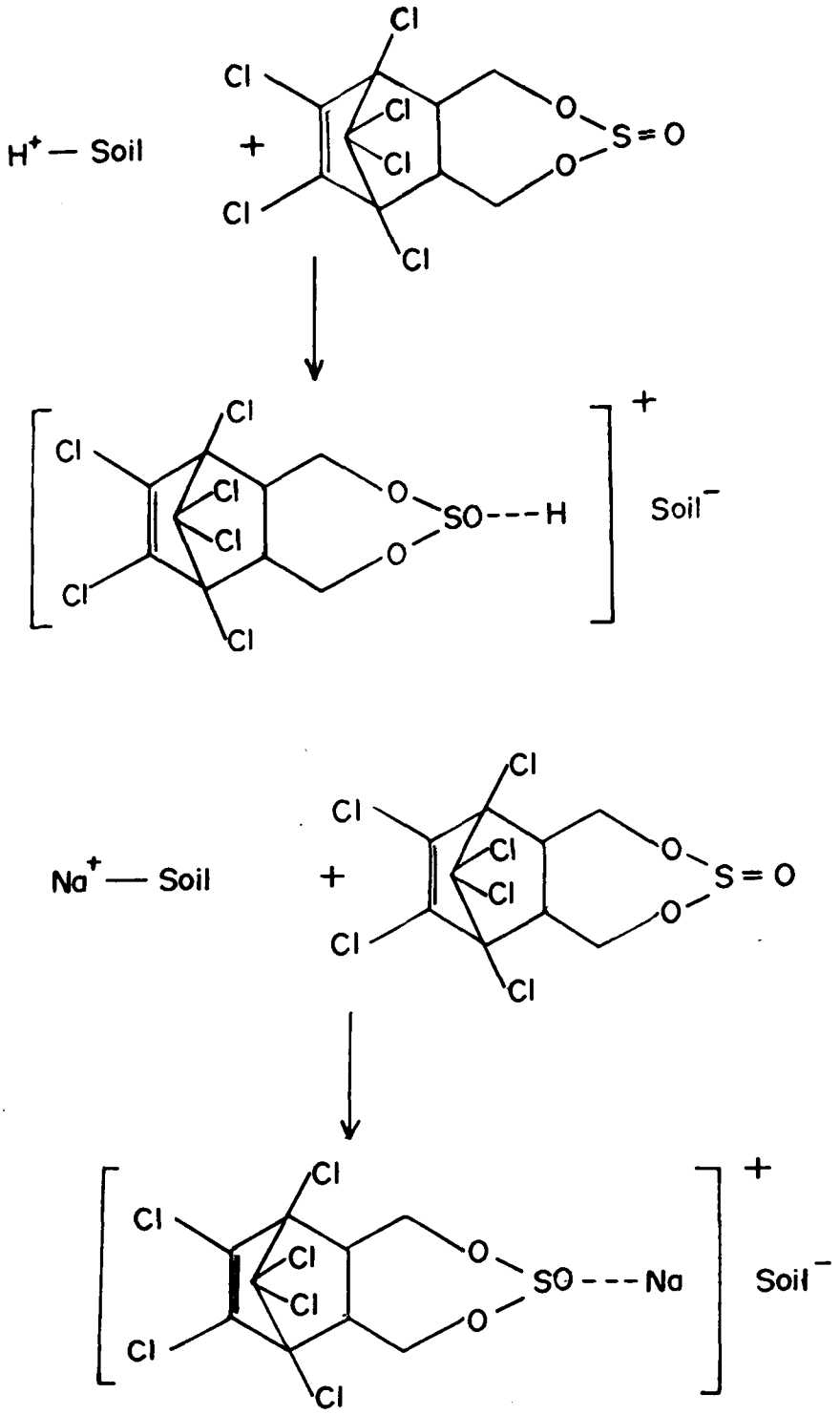
surfactant > Natural soil at 40°C, for both sandy loam (Mukteshwar) and silt clay loam (Bhopal) soils. The adsorption isotherms (Figs. 4.1 and 4.2) clearly indicate that endosulphan adsorption was higher in sandy loam (Mukteshwar) soil than in silt clay loam (Bhopal) soil. The higher adsorption on sandy loam soil (Mukteshwar) soil may be due to greater amount of organic matter in sandy loam (Mukteshwar) soil and other variations in soil properties. The S-shaped adsorption isotherms for all the treatments/effects also suggest that the adsorption was probably due to marked localisation of forces of attraction over the > S = 0 group of endosulphan leading to interaction with soil sites. The adsorption behaviour of endosulphan in all the studies for the two soils was fitted to the Freundlich equation

$$x/m = K\,Ce^{1/n} \qquad \ldots.(2)$$

where K and n are two empirical adsorption constants determined from the intercept and slope, respectively of the straight line (Figs. 4.3-4.4). The Freundlich constants K is a measure of the strength of adsorption (table 4.24-4.25) with the order of adsorption, that is, Hydrogen saturated soil > Sodium

saturated soil > Natural soil at 10°C > Natural soil at 20°C > Soil with 0.1% Non-ionic Surfactant > Soil from which organic matter was removed > Soil with 0.1% anionic surfactant > Natural soil at 40°C confirming with the K values. The Freundlich isotherms are shown in Figs. 4.3-4.4. The Freundlich constant 1/n provides an idea of intensity of adsorption which varies with the nature of the adsorbate for a given adsorbent; 1/n also indicates the degree of linearity between solution equilibrium concentration and adsorption. The values of K and 1/n are presented in tables 4.24, 4.25. The statistical average of Kd values (tables 4.24, 4.25) also confirms the above order of adsorption.

The mechanism of endosulphan interaction on Hydrogen saturated and Sodium saturated soils could be due to protonation or coordination. The expected mechanism is represented in scheme I. Comparisons of the adsorption of endosulphan on Hydrogen saturated soils with that on Sodium saturated soils revealed that higher adsorption was obtained on Hydrogen saturated soils (Figs. 4.1 and 4.2). The higher adsorption on Hydrogen saturated soils than on Sodium saturated soils may be due to the lower pH of the



Scheme —1

Hydrogen saturated soils. The results are in accordance with the work of Dregne et al. (1969), Singhal and Singh (1978), Supak et al. (1976), Singh et al. (1981) and Sharma et al. (1985), [23-27], who also observed higher adsorption of 2,4-D-dimecron, aldicarb and oxamyl on Hydrogen saturated soils and lower movement of pesticides in Hydrogen saturated soils. The weak adsorption on Sodium saturated soils in contrast to the strong adsorption on Hydrogen saturated soils further confirms the above interaction. Reduced adsorption in Sodium saturated soils may be due to non-availability of protons at higher pH and the presence of competing basic ions on the soil surfaces. A smaller number of exchange sites appear to be occupied in the sodium system than in the hydrogen system.

The adsorption affinity of endosulphan, on soils from which organic matter had been removed, observed a considerable decrease (Figs. 4.1, 4.2) in both soils compared with the adsorption of endosulphan on natural soils at 10°C and 20°C. The decrease in adsorption was mainly due to the decrease in the adsorptive capacity of the soils by oxidation of organic matter. This indicates that adsorptive

surfaces of organic matter have a greater capacity to retain the added endosulphan because organic matter itself acts as an adsorbent. The specific adsorptive capacity for organic matter (K_{om}) and the clay content (K_c) of the two soils were evaluated by dividing the distribution coefficient (statistical Kd) values by the organic matter and clay content present in the soil [20]. The values are given in tables 4.24, 4.25.

Examination of K_{om} and K_c values (Tables 4.24, 4.25) revealed that silt clay loam (Bhopal) soil had higher K_{om} values than the sandy loam (Mukteshwar) soil because silt clay loam (Bhopal) soil contains less organic matter. Hamaker and Thompson, 1972 [28], proposed that this tendency is due to the fact that organic matter may be responsible for making a significant contribution to the adsorption. The present study shows that endosulphan adsorption was attributed to organic matter which gave high K_{om} values. The results are in accordance with the work of Wahid and Sethunathan, 1978 [29], who demonstrated that beyond 2% organic matter in soils the adsorption of Parathion takes place almost entirely on organic surfaces, but at organic matter

content levels below 2% adsorption is significant on clay or inorganic surfaces.

The adsorption of endosulphan in presence of 0.1% non-ionic surfactant was higher than the adsorption on the soil from which organic matter was removed but in the case of 0.1% anionic surfactant adsorption was lower than the soil from which organic matter was removed. However, adsorption of endosulphan in presence of both the surfactants was lower than the natural soil at 20°C.

When the effect of temperature on adsorption of endosulphan on soils are compared, it is clear that isotherms reflect that adsorption of endosulphan decreases with a rise in temperature, as expected from the exothermic nature of the adsorption process. The lower adsorption of endosulphan at higher temperatures is partly due to the weakening of attractive forces between endosulphan and soil sites and partly due to enhancement of thermal energies of adsorbate, thus making the attractive forces between endosulphan and soil sites sufficient to retain endosulphan. However, the nature of the reaction remains unaffected in both the soils.

Thermodynamic parameters such as standard free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes, for adsorption of endosulphan were evaluated from the equations

$$\Delta G° = -RT \ln K_o \qquad ....(3)$$

$$\ln \left[\frac{K_{T_2}}{K_{T_1}}\right] = -\frac{\Delta H°}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad ....(4)$$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \qquad ....(5)$$

To obtain the thermodynamic equilibrium constant K_o, values of $\ln \frac{Cs}{Ce}$ are plotted against Cs followed by extrapolation to Cs = 0 as described by Biggar and Cheung [21]; where Cs is the surface concentration of endosulphan in m.mol/gm of soil and Ce the concentration of endosulphan in equilibrium suspension in m.mol/ml. Cs were calculated by using the relation

$$Cs = \frac{(\rho/M)\, A}{\frac{S}{N \cdot \frac{x}{m}}} \qquad ....(6)$$

where ρ, M and A are the density, molecular weight and cross-sectional area of the solvent,

respectively; S is the surface area of the adsorbent and x/m is the amount of endosulphan adsorbed, N is Avogadro's number. The cross-sectional area of the solvent A, is estimated from the equation

$$A = 1.091 \times 10^{-16} \left[\frac{M \times 10^{24}}{N \times \rho} \right]^{2/3} \quad \ldots(7)$$

The values of Cs, $\ln \frac{Cs}{Ce}$ are presented in tables 4.18-4.23. The values of thermodynamic parameters obtained from equations 3 to 7 are summarized in table 4.26.

The higher values of the thermodynamic equilibrium constant (K_o) table 4.26, at 10°C than at 20°C and 40°C again confirms that both soils had lower preference for endosulphan at 40°C as compared to 20°C and 10°C. The negative values of standard free energy changes ($\Delta G°$) table 4.26, indicates that reactions are spontaneous with high affinity for endosulphan. Negative values of standard enthalpies ($\Delta H°$) table 4.26, indicates that endosulphan and soil interactions are exothermic and products are energetically stable. The positive values of standard entropy changes ($\Delta S°$) table 4.26, recorded indicates

the stability of the soil endosulphan complex in the system. These studies demonstrated the higher adsorption of endosulphan in sandy loam (Mukteshwar) soil than in silt clay loam (Bhopal) soil. Endosulphan exhibited maximum affinity for Hydrogen saturated soil followed by Sodium saturated soil, Natural soil at 10°C, Natural soil at 20°C, Soil with 0.1% Non-ionic surfactant, Soil from which organic matter was removed, Soil with 0.1% Anionic surfactant and Natural soil at 40°C.

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CHAPTER V

THIN LAYER CHROMATOGRAPHIC MOVEMENT OF SOME SELECTED PESTICIDES ON DIFFERENT TYPES OF SOILS

V.1 INTRODUCTION

The movement of pesticides in soil affects their ability to effectively control the targeted pests and determines whether or not their use may lead to an environmental impact. Movement of pesticides has been generally estimated by using soil thin layer chromatographic techniques. Helling and Turner [1] introduced soil thin layer chromatographic technique as an alternate procedure for rapid, reproducible and expensive assessment of pesticide movement in soils. Some progress has been made in this technique in detail by autoradiography. Singh et al. [2-4] and Sharma et al. [5-8] have studied the movement of certain pesticides on soil thin layer chromatographic plates and the movement was expressed in terms of R_f values.

Several workers [9-17] have studied the movement of organohalogenated, organophosphorus and carbamate group containing pesticides on soils. In the present investigation movement of four different pesticides: Endosulphan, Chloropyriphos, Cypermethrin and Fenvalerate has been studied using soil thin layer chromatographic technique on six different

types of soils varying widely in their physico-chemical properties. Four different forms of each soil type namely - Natural Soil, Hydrogen Saturated Soil, Sodium Saturated Soil and Organic Matter Removed Soil were used for study. The solvent system used for thin layer chromatography was methanol-water (1:3). This system was studied because our studies presented in chapters III and IV of this thesis reveal (i) that all the pesticides under study have optimum movement on the soils, and (ii) these pesticides did not pose any problem in detection.

The data obtained are useful towards calculating the amount of irrigation/rainfall necessary to move the pesticides upto a depth of 60 inches of field soil with a view to examine the probability of its polluting the groundwater.

V.2 EXPERIMENTAL

V.2.1 Collection of soil samples : The surface soil samples (0-30 cms) were collected from Mukteshwar, Dehradoon (Doiwala), Tehri-Garhwal, Aligarh, Jhansi and Pilibhit districts of Uttar Pradesh, India, respectively. The soils were dried, crushed and sieved to obtain a small and nearly homogeneous particle size.

The composition and physico-chemical properties of the respective soils were determined in the same manner as has been described in the experimental portion of chapter II of this thesis.

V.2.2 Reagents : Pesticides; Endosulphan, Chloropyriphos, Cypermethrin, Fenvalerate used for soil thin layer chromatography were obtained from Indo-Gulf Fertilizers and Chemicals Sultanpur, U.P., India. All other chemicals used were of analytical reagent grade.

V.2.3 Soil thin layer chromatographic studies : Soil thin layer chromatographic plates of 0.5 mm thickness were prepared by spreading soil-water slurry on

10x20 cm clean glass plates with the help of applicator. After drying the plates, two lines at 3 cm and 13 cm above the base were scribed on the plates and pesticides were spotted on the plates. The plates were then developed in a solvent system of methanol and water in the ratio of 1:3 upto the upper line marked at 13 cm by ascending chromatography. A 2 cm wide strip of paper towel moistened with the developer was wrapped around the bottom of the plates to prevent disintegration of the soil layer when it comes in contact with the solvent system. Soil thin layer chromatographic plates were then taken out of the jar and allowed to dry. The movement of pesticides was then detected by keeping the air dried plates in iodine vapours sealed chamber. Brown coloured spots appear on the plates after some time depicting the movement of pesticides.

V.3 RESULTS

The composition and physico-chemical properties of the soils are presented in table 5.1. The mobilities of Endosulphan, Chloropyriphos, Cypermethrin and Fenvalerate are expressed as R_f values in presence of methanol-water (1:3) mixture, used as developer, for Mukteshwar, Doiwala, Tehri, Aligarh, Jhansi and Pilibhit soils and their different forms. The R_f values are presented in tables 5.2 to 5.5.

R_f values was calculated using the relation

$$R_f = \left[\frac{R_L + R_T}{2}\right] \qquad \ldots(1)$$

where R_L is the R_f of the leading front and R_T is the R_f of the trailing front. Line sketch of a typical movement is shown in Fig. 5.1

Table 5.1

Composition and Physico-chemical properties of the soils

Properties	Mukteshwar	Doiwala	Tehri	Aligarh	Jhansi	Pilibhit
% Sand	59.12	29.10	50.20	64.10	45.85	54.37
% Silt	34.80	59.90	30.80	26.40	38.15	32.13
% Clay	6.00	11.00	19.00	9.50	16.00	13.50
Texture	Sandy Loam	Silt Loam	Loam	Sandy Loam	Loam	Sandy Loam
pH	6.0	7.7	6.3	7.9	8.5	9.0
Electrical Conductance ($S\ m^{-1}$)	2.833×10^{-4}	1.387×10^{-4}	0.56×10^{-4}	4.88×10^{-4}	3.92×10^{-4}	3.14×10^{-4}
% Organic Matter	4.06002	1.8360	1.1895	1.0601	0.5948	0.3461
% Organic Carbon	2.355	1.0649	0.6899	0.6152	0.3450	0.2008
% $CaCO_3$	4.75	6.25	2.65	0.45	4.35	0.45
Cation Exchange Capacity [C mol P^+ Kg^{-1}]	17.00	5.90	5.80	4.90	8.50	4.70
Surface Area [m^2/gm]	58.979	200.53	234.96	100.40	100.00	34.80
Bulk Density	1.18	1.38	1.56	1.61	1.49	1.37
Porosity	0.33	0.43	0.38	0.33	0.39	0.46

Table 5.2

Movement of Endosulphan in different Soils and their different forms

Soil Form	R_f values					
	Mukteshwar	Doiwala	Tehri	Aligarh	Jhansi	Pilibhit
Hydrogen Saturated Soil	0.11	0.16	0.20	0.22	0.24	0.26
Sodium Saturated Soil	0.13	0.19	0.23	0.24	0.27	0.29
Natural Soil	0.17	0.20	0.24	0.28	0.32	0.33
Organic Matter Removed Soil	0.21	0.26	0.30	0.33	0.35	0.38

Table 5.3

Movement of Chloropyriphos in different Soils and their different forms

Soil Form	R_f values					
	Mukteshwar	Doiwala	Tehri	Aligarh	Jhansi	Pilibhit
Hydrogen Saturated Soil	0.24	0.27	0.31	0.35	0.37	0.40
Sodium Saturated Soil	0.28	0.30	0.36	0.40	0.42	0.45
Natural Soil	0.30	0.32	0.40	0.45	0.47	0.49
Organic Matter Removed Soil	0.33	0.37	0.42	0.49	0.51	0.52

Table 5.4

Movement of Cypermethrin in different Soils and their different forms

Soil Form	R_f values					
	Mukteshwar	Doiwala	Tehri	Aligarh	Jhansi	Pilibhit
Hydrogen Saturated Soil	0.17	0.19	0.21	0.23	0.24	0.26
Sodium Saturated Soil	0.19	0.21	0.24	0.27	0.29	0.31
Natural Soil	0.20	0.24	0.26	0.30	0.32	0.35
Organic Matter Removed Soil	0.23	0.28	0.31	0.35	0.38	0.41

Table 5.5

Movement of Fenvalerate in different Soils and their different forms

Soil Form	R_f values					
	Mukteshwar	Doiwala	Tehri	Aligarh	Jhansi	Pilibhit
Hydrogen Saturated Soil	0.18	0.21	0.22	0.25	0.28	0.31
Sodium Saturated Soil	0.22	0.24	0.26	0.27	0.32	0.35
Natural Soil	0.25	0.28	0.31	0.32	0.36	0.40
Organic Matter Removed Soil	0.27	0.30	0.33	0.36	0.42	0.44

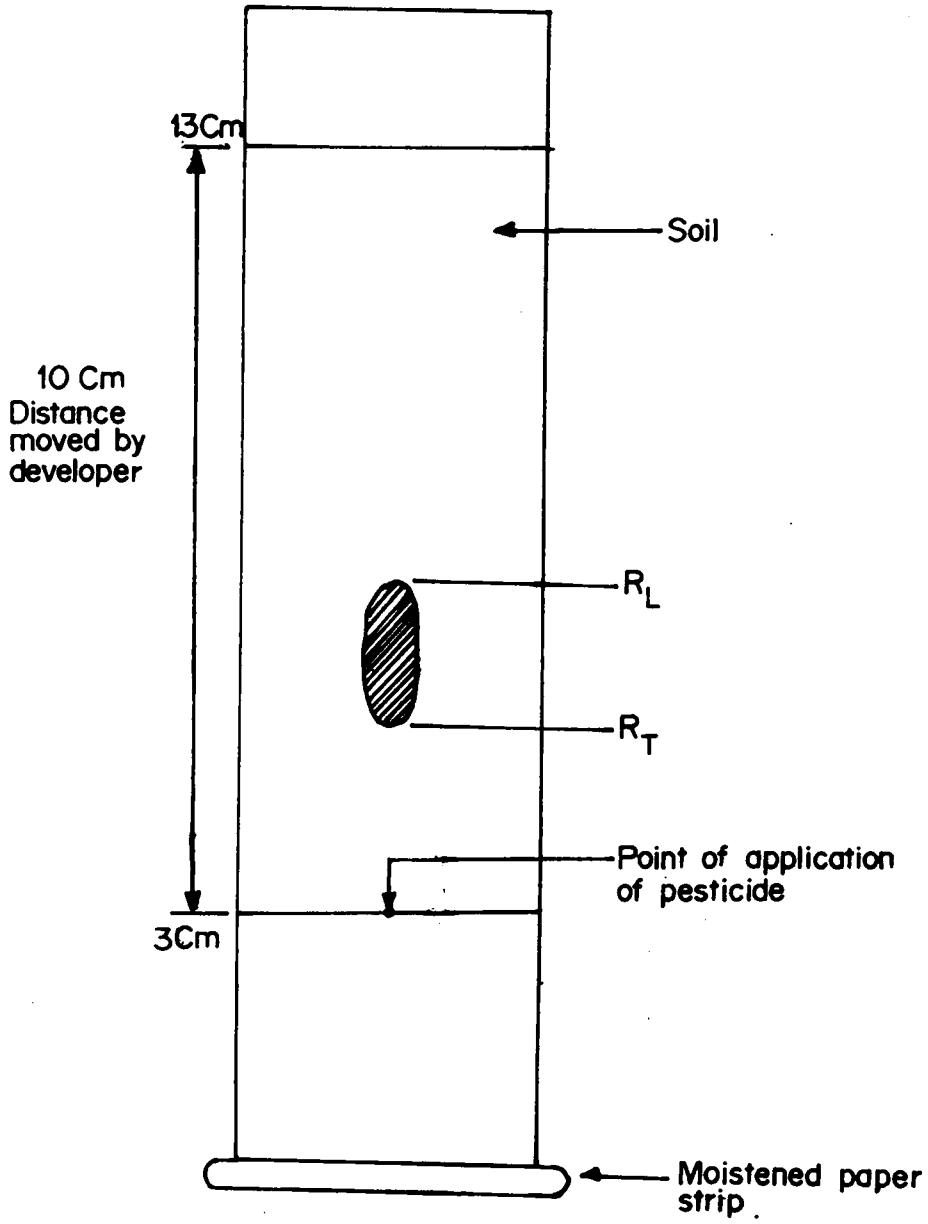

Fig.5.1: Soil TLC Plate.

Movement of pesticide in methanol – water (1:3) system.

V.4 DISCUSSION

It is clear from table 5.1 that the various soil samples varied widely in their composition and physico-chemical properties, this has great significance as it affects their movement which in turn affects the pesticides ability to effectively control the targeted pests and determine whether or not their use may lead to an environmental impact.

On studying table 5.2 it is clear that (i) the movement of Endosulphan, in other words the R_f value for Endosulphan is least in Mukteshwar soil and highest in Pilibhit soil. R_f values follow the following order - Mukteshwar < Doiwala < Tehri < Aligarh < Jhansi < Pilibhit. (ii) R_f value is least in hydrogen saturated soil and highest in organic matter removed soil with the order of movement being hydrogen saturated soil < sodium saturated soil < natural soil < organic matter removed soil.

The movement of other pesticides Chloropyriphos, Cypermethrin and Fenvalerate follows the same order as Endosulphan with Mukteshwar soil having the lowest R_f value and Pilibhit soil the highest R_f value. The R_f values are presented in tables 5.3-5.5.

This difference in the movement of pesticides in different soils and their different forms is due to the nature and properties of the pesticides and on certain soil properties such as organic matter content, clay content, texture and structure of the soil, porosity, pH and cation exchange capacity [18-22] of the soil.

The movement of pesticides was less in Mukteshwar soil as compared to other soils because it is of a much more fine texture then other soils as a result the equilibrium of pesticide between water and the interior soil aggregates becomes slower with increasing aggregate size and relatively small zone of pest control. R_f value of Doiwala soil is higher than Mukteshwar soil since the former is a coarse textured soil, but as it also contains large amounts of silt R_f value is less than other soils. The fineness of the soil texture decreases from Mukteshwar to Doiwala, to Tehri, to Aligarh, to Jhansi, to Pilibhit, which accounts for the R_f values increasing from Mukteshwar to Doiwala, to Tehri, to Aligarh, to Jhansi, to Pilibhit which confirms are results that the movement of pesticides is least in Mukteshwar soil and highest in Pilibhit soil.

The organic matter content of a soil is a very important factor which affects the movement of pesticides in soils. Greater the percentage of organic matter in the soil more will be their adsorption and lesser will be their mobility. The percentage of organic matter content follows the order (table 5.1) - Mukteshwar > Doiwala > Tehri > Aligarh > Jhansi > Pilibhit which confirms our results that movement of pesticides follows the order - Mukteshwar < Doiwala < Tehri < Aligarh < Jhansi < Pilibhit in the soils, with the least movement being in Mukteshwar soil and the highest in Pilibhit soil. This also confirms are results that organic matter removed soils show the highest degree of movement of pesticides in soils.

Another factor which again confirms our results is the low solubility of these pesticides [23] in water. The low solubility in water coupled with percentage of organic matter content and other factors such as soil texture and structure results in less movement.

Yet another factor which confirms our results is the cation exchange capacity of the soils. Generally, as a rule, higher the capacity of the soil less will be the movement. It is clear from table 5.1

that Mukteshwar soil has the highest capacity which alongwith other favourable factors results in less movement of pesticides and consequently the least R_f. A notable exception is the Jhansi soil which has a capacity second only to Mukteshwar soil but due to other factors such as coarseness of the soil and a low percentage of organic matter content there is no significant effect on the movement of pesticides.

The pH of a soil also affects the movement of pesticides [19]. Generally, soils with low pH show less movement of pesticides. This is in accordance of our results as Mukteshwar soil has the lowest pH and shows the least R_f values whereas Pilibhit soil has the highest pH and shows the highest degree of movement of pesticides, with the other soils lying in between the two limits. This also confirms that hydrogen saturated soils show the least movement of pesticides compared to other forms.

All other factors being equal pesticides show a greater degree of movement through more porous soils. The formulation in which a pesticide is applied may also influence its mobility to a certain extent.

All these factors confirms our results and lead us to the conclusion that - (i) Mukteshwar soil

shows the lowest degree of movement of pesticides and consequently has the lowest R_f value, followed by Doiwala soil, followed by Tehri soil, followed by Aligarh soil, followed by Jhansi soil, followed by Pilibhit soil. (ii) These factors also confirm that pesticides are transported to a lesser degree in hydrogen saturated soil consequently they have the lowest R_f value, followed by sodium saturated soil, followed by natural soil and finally the organic matter removed soil which shows the highest degree of movement of pesticides and has the highest R_f values.

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